PB87-145751

Treatment Alternatives for Controlling Chlorinated Organic Contaminants in Drinking Water

Thornton, CO

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jan 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-145751

EPA/600/2-87/011
January 1987

TREATMENT ALTERNATIVES FOR CONTROLLING CHLORINATED ORGANIC CONTAMINANTS IN DRINKING WATER

by

Mark A. Speed and Annette Barnard
City of Thornton
Thornton, Colorado 80229

Richard P. Arber, George C. Budd, and Frank J. Johns, II
Richard P. Arber Associates
Denver, Colorado 80206

Cooperative Agreement No. CR-809333-01

Project Officer

Ben W. Lykins, Jr.
Drinking Water Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-87/011	2.	3. RECIPIENT'S ACCESSION NO. PB87 145751/AS
4. TITLE AND SUBTITLE Treatment Alternatives for Controlling Chlorinated Organic Contaminants in Drinking Water		5. REPORT DATE January 1987
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Mark A. Speed, Annette Barnard [1] Richard P. Arber, George C. Budd, Frank Johns, II [2]		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS 1. City of Thornton 9500 Civic Center Drive, Thornton, CO 80229 2. Richard P. Arber Associates 44 Cook Street, Suite 300, Denver, CO 80206		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. CR-809333-01
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory-Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Research 10/81-9/85
		14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Ben W. Lykins, Jr. (com 569-7460/FTS 684-7460)

16. ABSTRACT

A pilot plant study was conducted by the City of Thornton, Colorado, to evaluate techniques for controlling chlorinated organic compounds formed in drinking water as a result of breakpoint, or free, chlorination. The pilot plant was operated for 46 months using the raw water sources available to the City's 20-mgd Columbine Water Treatment Plant. The treatment techniques evaluated included conventional coagulation and sedimentation, adsorption of organic precursors on powdered activated carbon (PAC), adsorption of chlorinated organic compounds on granular activated carbon (GAC), and alternative methods of disinfection, including the use of chloramines and chlorine dioxide in addition to the present practice of breakpoint chlorination. The effectiveness of the alternatives were assessed with respect to formation or removal of total trihalomethane (TTHM) and total organic halogen (TOX). In addition, the alternative disinfectants were evaluated for biocidal effectiveness. Based on the study findings, a process that employs chlorine dioxide in combination with chloramination was selected for full-scale evaluation. Neither GAC nor PAC was found to be capable of consistent or reliable control of TTHM or TOX. The method of chloramination affected the extent of TTHM and TOX formation and of bacteria inactivation. The method that resulted in the lowest concentration of these chlorinated organic compounds had the lowest biocidal efficiency as well, and therefore was not considered acceptable. A raw water monitoring program was conducted concurrently with the pilot plant program. Certain raw water sources exhibited a chlorine dosage dependency toward TTHM formation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 195
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

The information in this document has been funded in part by the U.S. Environmental Protection Agency under Cooperative Agreement No. CR-809333-01 to the City of Thornton, Colorado. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report discusses a pilot plant program that was undertaken to investigate treatment alternatives for controlling chlorinated organic contaminants. Alternatives that were evaluated included adsorption of organics on granular activated carbon and powdered activated carbon and alternative methods of disinfection, including free chlorination, chloramination, and the use of chlorine dioxide.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

A pilot plant study was conducted by the City of Thornton, Colorado, to evaluate techniques for controlling chlorinated organic compounds formed in drinking water as a result of breakpoint, or free, chlorination. The pilot plant was operated for 46 months using the raw water sources available to the City's 20-mgd Columbine Water Treatment Plant. The treatment techniques evaluated included conventional coagulation and sedimentation, adsorption of organic precursors on powdered activated carbon (PAC), adsorption of chlorinated organic compounds on granular activated carbon (GAC), and alternative methods of disinfection, including the use of chloramines and chlorine dioxide in addition to the present practice of breakpoint chlorination. The effectiveness of the alternatives were assessed with respect to formation or removal of total trihalomethane (TTHM) and total organic halogen (TOX). In addition, the alternative disinfectants were evaluated for biocidal effectiveness.

Based on the study findings, a process that employs chlorine dioxide in combination with chloramination was selected for full-scale evaluation. Neither GAC nor PAC was found to be capable of consistent or reliable control of TTHM or TOX. The method of chloramination affected the extent of TTHM and TOX formation and of bacteria inactivation. The method that resulted in the lowest concentration of these chlorinated organic compounds had the lowest biocidal efficiency as well, and therefore was not considered acceptable.

A raw water monitoring program was conducted concurrently with the pilot plant program. Certain raw water sources exhibited a chlorine dosage dependency toward TTHM formation. Procedures were instituted for determining the TTHM formation potential (TTHMFP) that should be considered when analyzing for TTHMFP.

This report summarizes work conducted under Cooperative Agreement No. CR-809333-01 by the City of Thornton under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from October 1, 1981 to July 31, 1985, and work was completed as of July 31, 1985.

CONTENTS

Foreword iii
Abstract iv
Figures vii
Tables ix
Acknowledgment x

1. Introduction 1

2. Conclusions 2

3. Recommendations 4

4. Literature Review 5
   General 5
   Nitrogen Removal Processes 6
   Trihalomethanes 8
   By-Products of Chlorination Other Than Trihalomethanes 12
   Treatment Methods For Trihalomethanes 14
   Alternative Disinfectants 15

5. Background 20
   Raw Water Quality 20
   Treatment 21
   Pilot Plant Program 23

6. Pilot Plant 25
   Program 25
   Results 43

7. Raw Water Monitoring 74
   Program 74
   Results 80

8. Batch Studies of Chlorination Characteristics . . 84
   General 84
   Methods 84
   Results 84
   Summary 92

References 95

Appendices

A. Evaluations of Critical Experimental Parameters 101
B. Raw Water Monitoring Results 106
C. Final Report - Significance of Organic Amino Nitrogen Compounds in Raw Water from Thornton, Colorado 147

FIGURES

Number		Page
1	Columbine Water Treatment Plant processes	22
2	Pilot plant processes	26
3	Pilot plant modes of operation	28
4	Pilot plant sample points	33
5	Columbine Water Treatment Plant sample points . . .	34
6	Performance comparison of pilot plant versus full-scale operation in regard to TOC	44
7	Performance comparison of pilot plant versus full-scale operation in regard to TTHM	45
8	Performance comparison of pilot plant versus full-scale operation in regard to terminal TTHM	46
9	Performance comparison of pilot plant versus full-scale operation in regard to TTHMFP	47
10	Performance comparison of pilot plant versus full-scale operation in regard to TOX	48
11	Performance comparison of pilot plant versus full-scale operation in regard to terminal TOX	49
12	GAC performance evaluation using TOC removal data for Mode 1 - Free Chlorination	53
13	GAC performance evaluation using TOC removal data for Mode 4 - Postammoniation	54
14	GAC performance evaluation using TTHM removal data for Mode 1 - Free Chlorination	55
15	GAC performance evaluation using TTHM removal data for Mode 4 - Postammoniation	56
16	GAC performance evaluation using TTHMFP removal data for Mode 1 - Free Chlorination	57
17	GAC performance evaluation using TTHMFP removal data for Mode 4 - Postammoniation	58
18	GAC performance evaluation using TOXFP removal data for Mode 4 - Postammoniation	60
19	Alternative disinfectant evaluation using TTHM formation data for Mode 1 - Free chlorination . . .	61
20	Alternative disinfectant evaluation using TTHM formation data for Mode 4 - Postammoniation	62
21	Alternative disinfectant evaluation using TTHM formation data for Mode 5 - Preformed chloramines .	63

22 Alternative disinfectant evaluation using TTHM formation data for Mode 6 - Dual Disinfection . . . 64
23 Alternative disinfectant evaluation using average instantaneous TTHM data 66
24 Alternative disinfectant evaluation using TOX formation data for Mode 1 - Free chlorination . 67
25 Alternative disinfectant evaluation using TOX formation data for Mode 4 - Postammoniation 68
26 Alternative disinfectant evaluation using TOX formation data for Mode 5 - Preformed chloramines . 69
27 Alternative disinfectant evaluation using TOX formation data for Mode 6 - Dual Disinfection . . . 70
28 Alternative disinfectant evaluation using average instantaneous TOX data 71
29 Alternative disinfectant evaluation using standard plate count data 73
30 Raw water sample points 76
31 TTHM and TOX formation characteristics along breakpoint curve for Thornton raw water 86
32 TTHM formation characteristics along breakpoint curve for various Metropolitan Denver raw sources 87
33 TTHM and DCAN formation characteristics along breakpoint curve for Thornton raw water 89
34 TTHM and organic chloramine formation characteristics along breakpoint curve for Thornton raw water . . . 90
35 Alternative chlorination schemes on breakpoint curve 91
36 Comparison of alternative chlorination schemes . . 94

TABLES

Number Page

1 Pilot Plant Sample Points 31
2 Full Scale and Pilot Plant Sampling Schedule . . . 35
3 Collection, Preservation, and Storage of Samples . 36
4 Analytical Procedures 40
5 Instrumentation 42
6 Raw Water Sample Points 75
7 Standley Lake Series Sample Points 78
8 Raw Water Monitoring Sampling Schedule 79
9 Standard Plate Count of Alternative Chlorination Schemes 92

ACKNOWLEDGEMENTS

Sincere appreciation is expressed to the Thornton City Council, Utilities Board, and Utilities Department staff for their concern for the quality of water provided to the customers as seen through their support of the pilot plant project. The City of Thornton funded over 80 percent of the project costs.

Thanks also to Ron Ewig and the other operators from the Columbine Water Treatment Plant responsible for the operation of the pilot plant. A special note of thanks goes to Annette Barnard, Jim Gindleberger, and the laboratory staff for conducting the sampling, analytical and quality assurance programs.

SECTION 1

INTRODUCTION

Because of concern for the quality of water that it provides to its customers, the City of Thornton, Colorado, has undertaken detailed pilot plant investigations to assess approaches for controlling organic contaminants while retaining the basic function of water treatment for providing a product that is free of disease-causing organisms. The project was initiated to determine the extent of formation of chlorinated organic compounds as a result of the use of breakpoint chlorination for oxidation of ammonia, and to evaluate techniques for controlling these compounds. The pilot plant was operated for 46 months using the raw water sources available to the City's 20 MGD Columbine Water Treatment Plant. Alternatives that were evaluated included adsorption of organics on granular activated carbon (GAC) and powdered activated carbon (PAC) and alternative methods of disinfection, including the use of chloramines and chlorine dioxide in addition to the present practice of breakpoint chlorination. Evaluations were performed to assess the effectiveness of the alternatives with respect to formation or removal of total trihalomethanes (TTHM), formation or removal of total organic halogen (TOX), and biocidal efficiency.

Based on the findings of this study, a process that employs chlorine dioxide in combination with chloramination was selected for full-scale evaluation. Neither GAC nor PAC was found to be capable of consistent or reliable control of TTHM or TOX. An additional finding of the study was that the method of chloramination affected the extent of formation of TTHM and TOX. The best approach for reducing the formation of these chlorinated organics consisted of forming chloramines before their addition to the main flow stream.

Since the raw water contains the precursors for TTHM and TOX formation, a raw water monitoring program was conducted concurrent to the pilot plant program. The purpose of the raw water monitoring program was to characterize the water sources available to Thornton. Based upon the characterizations, the City of Thornton can compare the quality of the various sources to one another, recognize the annual changes in quality for each source, and plan their raw water supplies based on water quality.

SECTION 2

CONCLUSIONS

1. The quality of the Thornton, Colorado, raw water varies during the year and follows a fairly predictable annual cycle.

2. The raw water sources for the Columbine Water Treatment Plant exhibit a chlorine dosage dependency with respect to TTHM formation.

3. A literature review shows that TTHM formation can be related to algae concentrations in the raw water. A study conducted during the pilot plant program showed that TTHM produced by chlorination of proteins can be significant during summer months of high algae growth. TTHM is only one example of organohalogen compounds that can be produced by chlorination of proteins. Algae can be a significant source of these proteins.

4. Compared to a conventional coagulation and sedimentation process, PAC doses of 5 to 10 mg/L had a minimal effect on the removal of organics as measured by total organic carbon (TOC). TOC removal was approximately 6 percent greater with PAC than without it. PAC addition did not effect the TTHM and TOX concentrations in the filter effluent.

5. GAC is capable of removing TTHM and TOX. These chlorinated organics reached a steady state concentrations in the effluent from the GAC columns, with breakthrough occurring at certain intervals. The interval of time to breakthrough was not long enough for GAC to be an economical alternative to using other disinfectants for controlling TTHM and TOX.

6. The conventional treatment processes could remove approximately 30 to 40 percent of the trihalomethane formation potential (TTHMFP). By moving the point of chlorination downstream of conventional treatment, a decrease in TTHM formation was realized. However, the precursor removal by sedimentation was not adequate to consistently allow Thornton to produce water with less than

100 ug/L TTHMFP.

7. Alternative chlorination schemes can be characterized by the region in which the chlorine species occur along the breakpoint chlorination curve. Each chlorination scheme results in different water quality in terms of bacteria and chlorinated organic byproducts.

   Four alternative chlorination schemes involved chloramines: Chlorine addition to form monochloramines, chlorine addition to form dichloramines, post-ammoniation chlorination, and chloramination by addition of a chloramine solution. The chloramination procedure affects the amount of disinfection and the byproduct formation even when the water following chloramination contains the same type and concentration of chloramines.

8. Selection of the disinfection scheme should be based on two primary criteria: Disinfection capabilities and disinfection byproduct formation. The goal is to maximize disinfection (i.e. to kill bacteria and other pathogens) and to minimize the formation of byproducts that have potentially adverse health effects.

9. None of the alternative chlorination schemes produced both effective disinfection and minimal formation of chlorinated organic byproducts, as indicated by TTHM and TOX, during the pilot plant study. The chlorination schemes that maximized disinfection were those that resulted in higher byproduct concentrations. Those schemes that minimized byproduct formation had a smaller degree of bacteria kill.

10. The use of chlorine dioxide as a disinfectant maximized bacteria kill and minimized the formation of chlorinated organic byproducts. However, because the chlorine dioxide residual is limited by chlorite and chlorate formation, a chlorine or chloramine solution must be added so that a disinfectant residual can be maintained in the distribution system.

SECTION 3

RECOMMENDATIONS

1. The raw water monitoring program should be continued to develop the data base further. The program will allow for evaluation of water sources and provide data for further evaluation of the variability of the supply on an annual basis.

2. The evaluation and eventual design of a full-scale chlorine dioxide generation and feed system should be considered for the Columbine Water Treatment Plant.

3. Alternative chlorination schemes should be evaluated for a water supply containing a low ammonia concentration. The disinfection and byproduct formation results for a low-ammonia water may be different than those found during this pilot plant study. Thornton's raw water supply from Standley Lake can be considered a low-ammonia water, but those supplying the Columbine Water Treatment Plant and the pilot plant are moderate-to high-ammonia waters.

4. When evaluating alternative disinfectants, water utilities should consider more parameters than those currently regulated under the U.S. Environmental Protection Agency Primary Drinking Water Standards. Other parameters can provide a broader indication of disinfection byproducts and bacteriological quality. For example, when considering chloramines as an alternative to free chlorine, TOX should be used along with TTHM as a minimum indication of byproduct formation. A more sensitive indicator of bacteriological quality, such as heterotrophic plate count, should be used along with the total coliform count.

5. Because different waters have different characteristics in relation to TTHM formation, certain parameters should be monitored and reported when analyzing for TTHMFP. These parameters include free and total chlorine residuals, pH, temperature, and storage period. In addition, since some waters exhibit a dosage dependency toward TTHM formation, TTHMFP analyses should be conducted for at least two different chlorine dosages.

SECTION 4

LITERATURE REVIEW

GENERAL

Like many other communities, the City of Thornton is confronted with questions that relate to disinfection of their water supply. A number of issues must be evaluated when selecting the appropriate disinfection method. These include questions on the formation of disinfection by-products while maintaining the capability to attain adequate disinfection.

In recent years, the questions relating to disinfection by-products and their health effects have become significant issues within the water supply field. This concern has evolved from the finding that certain carcinogens or suspected carcinogens are ubiquitous in drinking water supplies, and that these compounds are associated with the practice of chlorination. Most notable among the compounds of concern are the trihalomethanes, which include, chloroform ($CHCl_3$), bromoform ($CHBr_3$), dibromochlormethane ($CHBr_2Cl$), and dichlorobromomethane ($CHBrCl_2$). At the present time, the trihalomethanes are the only disinfection by-products that are regulated under the U.S. EPA Primary Drinking Water Standards. This standard is based on a four quarter moving average, which is not to exceed 0.10 mg/L TTHM.

Although considerable attention has focused on TTHM, concern for other halogenated and nonhalogenated disinfection by-products has increased (NAS, 1980; Bull, 1982). Because many of the compounds that are formed in the disinfection process are chlorine substituted organics, interest in the surrogate parameter, TOX, has evolved.

As a consequence of the concerns for these disinfection by-products, interest in alternatives to the most commonly used disinfection approach, breakpoint chlorination, are being more frequently considered. These alternatives include chloramination, chlorine dioxide, and ozone. The latter two disinfectants are usually considered in combination with a terminal disinfectant. Each alternative must be evaluated with respect to potential health effects because of the formation of disinfection by-products, and its capability to achieve disinfection for a broad range of pathogenic organisms. In some cases, a given disinfection approach may minimize the formation of disinfection by-products of concern but may not achieve a desired level of disinfection when considering all of the pathogenic organisms that may be present.

In the case of Thornton, the problem of nitrogen in the raw water has been related to the overall issue of disinfection. Some of the raw water sources for the City contain high levels of ammonia and organic nitrogen. In the past, these forms of nitrogen degraded to yield high levels of nitrite (up to 2 mg/l) in the distribution system, if they were not removed by breakpoint chlorination. The high levels of chlorine required to achieve breakpoint chlorination resulted in the formation of undesireable concentrations of TTHM and TOX. As such, Thornton has undertaken the pilot plant program described in this report to evaluate alternative approaches for disinfecting its drinking water, organic removal, and dealing with the problem of nitrogenous compounds.

NITROGEN REMOVAL PROCESSES

High levels of nitrogen, primarily in the ammonia form at concentrations up to 9 mg/L, were found in some of the raw water sources for the Thornton water system. Several approaches were available for ammonia removal: breakpoint chlorination, nitrification and denitrification, ammonia stripping, and selective ion exchange.

Breakpoint Chlorination

Breakpoint chlorination is the most commonly used nitrogen removal method in water treatment practice. Removal actually occurs as an ancillary effect that is associated with the main objective of breakpoint chlorination, which is to provide free chlorine residual. An undesired effect can also occur because the high levels of chlorine required for breakpoint chlorination can result in the formation of high levels of trihalomethanes. As a consequence, many communities are investigating the use of alternatives to breakpoint chlorination for resolving the trihalomethane problem. The use of chloramines is being widely considered for such an alternative. However, Thornton has observed high levels of nitrite in their water distribution system when using chloramines. As a consequence, alternative methods for nitrogen removal may be required if suitable alternative disinfection approaches cannot be found for the breakpoint and chloramine methods. As discussed in the following, each of the alternative methods for nitrogen removal have significant disadvantages which must be considered.

Nitrification/Denitrification

Nitrification involves the biological oxidation of ammonia to nitrite and then from nitrite to nitrate by two groups of autotrophic bacteria, Nitrosomonas and Nitrobacter. Denitrification involves the reduction of nitrate to nitrite and then to nitrogen gas by a wide variety of facultative bacteria. Denitrification occurs under anoxic conditions and requires an organic energy source such as methanol, although the need for methanol may be eliminated under certain process schemes (Jorgensen, 1976). Both attached growth and suspended growth reactors have been used for biological nitrification and denitrification. Attached growth systems that are commonly employed are the trickling filter, the rotating biological contactor, and the packed bed reactor. In attached growth systems, the bacterial organisms become attached to a stone, wood, or plastic fixed media. Suspended growth processes, include activated sludge and oxidation ditch processes. These are more typically used for wastewater treatment and involve mixing of the wastewater with an aerated, suspended microbiological mass to provide a viable culture through recycling of sludge (Kenyon, 1979). Biological nitrification-denitrification involve moderate cost as compared with other nitrogen removal processes (Culp et al., 1978). However, these processes are considerably less efficient at colder temperatures and are difficult to control and automate. In addition, they are subject to upset and may not provide the reliability desired for a drinking water system.

Air Stripping

The removal of ammonia by the air stripping process is a modified application of the physical desorption process for removing dissolved gases from water. It is necessary for the ammonia to be in the unionized form, which is usually accomplished by raising the pH of the water. The stripping process consists of raising the pH of the water to the range of 10.8 to 11.5, then forming and reforming of water droplets in a stripping tower, and providing air-water contact and droplet agitation by circulation of large quantities of air through the tower (Culp et al., 1978). The transfer of ammonia gas takes place between the liquid and gaseous phase during droplet formation. The ammonia is then discharged into the atmosphere with the off-gases.

One approach to implementing the air stripping approach in a water treatment plant would be to use a lime softening approach for coagulation and sedimentation. This would achieve the increase in pH that is required for conversion to unionized ammonia.

The major problems associated with ammonia stripping are the decrease in efficiency at cold ambient air temperatures, the freezing potential when operating at temperatures below $32^{o}F$, and the potential for deposition of calcium carbonate scale from the unstable, high pH water onto the stripping tower media. Scale formation results in an efficiency loss associated with reduced air circulation and droplet formation (EPA, 1975).

Selective Ion Exchange

The selective ion exchange process utilizes the natural zeolite, clinoptilolite. It has the advantages of high removal efficiency and insensitivity to temperature fluctuations (EPA, 1975). However, the process is extremely complex and can be difficult to operate. In addition, it requires a high capital expenditure. Another major disadvantage to the selective ion exchange process is that a concentrated spent regenerant solution must be disposed unless a complex regenerant recovery system is used.

TRIHALOMETHANES

Trihalomethanes have been found to occur in drinking water as reaction products of chlorine, added for disinfection, and organic compounds present in the raw water source. Of the organic compounds that serve as precursors to the formation of trihalomethanes, naturally occurring humic materials are the most widely cited. These materials are degradation products of vegetation, much of which is of terestrial origin. In addition to humic materials of terrestrial origin, precursors can be derived from aquatic plants and wastewater discharges (Johnson and Jensen, 1983).

Soluble humic materials are generally categorized into the humic and fulvic acid fractions. Although there have been some efforts to define the character of these fractions, in reality, the definitions are operational and relate to the methods for extracting the respective fractions (Dempsey et al., 1984). Humic acid has been characterized as that portion of the soil organic matter that is soluble in alkaline solutions but forms a precipitate under acidic conditions. Fulvic acid is characterized by solubility under both alkaline and acidic conditions (NAS, 1980).

Beyond the differences in extraction methods, there are some general differences in the characteristics of the respective fractions. Fulvic acids are generally lower in molecular weight than humic acids and typically contain more oxygen and less nitrogen than the humic acid fraction in both soil and aquatic organic matter (Black and Christman, 1963).

Humic material is characterized by a polymeric structure which contains carboxyl and hydroxyl groups. Rook (JAWWA, 1976) emphasizes the importance of polyhydroxy aromatic rings within the humic materials with respect to reactions that form trihalomethanes. Specifically, the dihydroxy aromatic, resorcinol, is proposed by several investigators as a model compound for humic precursors to trihalomethane formation. Resorcinol is meta dihydroxy benzene. The meta dihydroxy configuration activates the aromatic structure for attack by chlorine (Boyce and Hornig, 1983). The result is a rapid reaction that results in the formation of trihalomethane.

Other compounds that can serve as precursors include ethanol, acetaldehyde, methyl ketones, and secondary alcohols (NAS, 1980). However, in the case of the simple ketones, several investigators have questioned the importance of their role as potential precursors under conditions found in water treatment plants (Stevens et al., 1978). Although the simple ketones do not readily react with chlorine, other types of compounds, including more complex ketones, may react more rapidly (NAS, 1980).

Arguello et al. (1979) evaluated chlorine reactions with a number of model compounds in addition to resorcinol and humic acid. Their work indicates that phenols and aromatic amines can react with chlorine to form chloroform under conditions of high pH, and that some aliphatic carbonyl compounds are also chloroform precursors.

The possibility for significant algal effects on trihalomethane formation has been suggested by a number of researchers (Oliver and Schindler, 1980; Briley et al., 1979, 1984; Hoehn et al., 1983a, 1983b). The work of Briley et al. (1979, 1984) suggests that significant levels of trihalomethane can be formed by Anabaena, Scenedesmus and Pediastrum at chlorophyll-a levels comparable to those found in raw water sources for Thornton. This work has been performed on pure algal cultures and it is clear from their results that algae represent a potentially significant source of trihalomethane precursors. Both algal cells and extracellular products that were excreted into the water column were found to contain precursor material. The characteristics of the formation potential varied depending on species. In some cases extracellular products yielded greater formation, whereas cellular material resulted in greater yields in other cases. The growth phase corresponding to maximum formation potential also varied between algae species.

Hoehn et al. (1983a, 1983b) evaluated the effect of biological activity on the potential for trihalomethane formation in a reservoir. The data show variations in primary algal productivity and the level of extracellular products on both a diurnal and annual basis. Although no definite relationships were demonstrated, they concluded that these variations may have an effect on trihalomethane formation and the yield of trihalomethanes from dissolved organic carbon. They also suggest that it is possible for algal growth phase, algal speciation, and heterotrophic activity to have an effect on formation potential. Because of these suspected complexities, they concluded that a direct correlation between THM formation potential and chlorophyll-a levels or other measures of algal mass may be simplistic. This would support a finding in their previous work (Hoehn et al., 1980) that a direct relationship between chlorophyll-a and trihalomethane formation potential could not be demonstrated. However, it should be noted that this does not imply a lack of an overall relationship between algal productivity and the formation of trihalomethane precursor compounds.

Wetzel (1983) indicates that although algal products may have short-term impacts on organic carbon fluxes in lakes, they tend to degrade rapidly and do not contribute substantially to the long-term organic carbon content of a lake. Apparently, this is the case for the precursor material formed in association with algae, since it has been reported to be relatively unstable and tends to fluctuate significantly over short periods of time (Briley et al., 1979, 1984; Hoehn et al., 1983a, 1983b). While algal sources of precursor material may contribute to the overall precursor pool over short periods of time, long-term contribution, as would be the case for humic materials, is less significant.

In the case of wastewater discharge, biological processes are used which can result in the formation of humic and fulvic acid degradation products that may serve as precursors. Additionally, industrial discharges can contain organic compounds that can serve as precursors (Boyce and Hornig, 1983). Therefore, the presence of wastewater effluents can have a significant effect on trihalomethane formation.

Several general observations have developed with respect to the nature of the reactions between precursors and chlorine in water treatment:

- pH - The reactions to form trihalomethanes appear to be catylized by hydroxide ions. Therefore, a dramatic increase in the rate of formation is typically observed with increased pH (AWWA, 1982).

- Temperature - As with many reactions the rate of trihalomethane formation is observed to significantly increase with temperature (AWWA, 1982).

- Halide Ion - The presence of halide ions, including fluoride, bromide, and iodide, can have an effect on the formation of trihalomethanes upon chlorination. These can result in formation of mixed halogen trihalomethanes and can increase the yield of trihalomethanes (AWWA, 1982). In particular, bromide ions are frequently found to be present and can have a significant effect on the yield of trihalomethanes (Amy et al., 1984).

- Chlorine Dose - Only a slight influence on trihalomethane formation typically occurs when free chlorine dose is increased beyond the demand (AWWA, 1982). While this may be true, Oliver and Schindler (1980) have reported that in the case of precursors of algal origin, a much greater chlorine dose dependancy is observed as compared with humic acids. Bromide has also been reported to affect chlorine dose relationships with trihalomethane formation (Minear and Bird, 1980). Therefore, caution must be exercised in generalizing with respect to the chlorine dose effect on the formation of trihalomethanes.

- Annual Cycle - Significant seasonal variations in yield of trihalomethane formation potential per quantity of organic carbon have been observed by several researchers. As an example, Veenstra and Schnoor (1980) observed a variation in trihalomethane yield for raw water from a reservoir in Iowa that ranged from 0.3 micrograms of trihalomethane formation potential per milligram of TOC in December to 20.2 micrograms of trihalomethane formation potential per milligram of TOC in late March and April. Generally, the observed yields were greatest from spring through summer and were substantially lowered during the winter. Similar results have been reported by Hoehn et al. (1980) for a reservoir in Virginia. Some of this seasonal variation has been attributed to differences in temperature. However, Veenstra and Schnoor (1980) felt that temperature was not much of factor for a reservoir in Iowa. Brett and Claverly (1979) observed that high trihalomethane formation potentials for a water system in England could occur during high flood conditions in the winter, thereby further suggesting that temperature may not be the only explanation. They observed variations in molecular weight distribution of dissolved organic carbon over an annual cycle that appeared to relate to the characteristics for trihalomethane formation.

In a given water, the occurrence of an array of precursor compounds is possible. Although some common characteristics are observed, care must be taken to avoid relying upon generalities in dealing with the problem of trihalomethane formation and it should be recognized that the characteristics of formation may vary with water source. This is illustrated by the finding that while the treatment of resorcinol and m-dihydroxybenzoic acid with potassium permanganate at low dosages provided nearly complete effectiveness in preventing the formation of trihalomethanes upon chlorination, potassium permanganate was only minimally (10% to 20%) effective in reducing the formation of trihalomethanes from precursors in Ohio river water (AWWA, 1982). Different effects may also be observed at different locations and during different times of the year.

BYPRODUCTS OF CHLORINATION OTHER THAN TRIHALOMETHANES

When chlorine is added to water, it proportionates according to the following reaction to form chloride (Cl^-) and hypochlorous acid (HOCl):

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl$$

HOCl reacts with organic compounds in one of three ways: addition reactions, substitution reactions, or oxidation reactions (NAS, 1980). Addition and substitution reactions result in the formation of chlorinated organic compounds through the addition or substitution of the Cl(+I) component of HOCl into organic structures. Oxidation reactions result in a change in the oxidation state of chlorine. While they account for most of the chlorine demand, the end products are typically not chlorinated organic compounds.

Several researchers have investigated the reactions between chlorine and humic materials to determine reaction products that occur in addition to trihalomethanes. Christman et al. (October, 1983) reported the formation of a number of chlorinated organic acids of which dichloroacetic and trichloroacetic acid were prominent. In fact, they observed that dichloroacetic acid could be found in greater concentration than chloroform. Kringstad et al. (1985) reported the formation of a number of chlorinated phenols upon chlorination of humic acid. In other work, Kringstad et al. (1983) observed the formation of chlorinated forms of acetones and aldehydes from the chlorination of humic acid. Coleman et al. (1984) used closed-loop stripping methods in conjunction with GC/MS and identified the following halogenated end products of the reaction between chlorine and humic acids: trihalomethanes, haloacetic acids, haloacetonitriles, halopropanones, halopropenals, halopropenenitriles, halopropenes, halophenols, and halothiophenes. They concluded that only a small fraction (about 6%) of the total mutagenic activity of the sample introduced to a gas chromatograph can be resolved by GC peaks, and observed that many non-volatile and/or labile compounds may go undetected with traditional gas phase methods. These compounds may be responsible for a majority of the mutagenic activity of chlorination byproducts. As such, the need for extensive derivatizition techniques to make the sample more susceptible to analysis by gas chromatography was suggested.

Because of the high nitrogen levels found in Thornton's water, the formation of organic and inorganic nitrogenous compounds is of interest to the project described in this report. In this regard, significant interest has emerged with respect to the haloacetonitriles (Bull, 1982). Scully et al. (1984) have reported the formation of a number of organic N-chloramines in chlorinated water as observed using high performance liquid chromotography.

In addition to halogenated species of chlorination byproducts, concern has been expressed for non-halogenated products that may contain aromatic or alicyclic structures. The health risks associated with these byproducts have not as yet been considered to a significant degree (NAS, 1980).

One of the significant problems that must be confronted in dealing with the question of chlorine byproducts is the difficulty encountered in analyzing for the array of chemical species that may be formed. It is estimated that as little as 10% of the measureable total organic carbon may be amenable to identification by conventional analytical methods (Bull, 1982; NAS, 1982). Of specific concern are compounds that are either nonvolatile or thermally labile, and thereby not subject to analysis with GC or GC/MS methods unless extensive derivitization techniques are used (Coleman et al. 1984). In an evaluation of health affects in surface waters in the Netherlands, Kool et al. (1982) reported that a nonvolatile compound had the greatest associated mutagenic activity and had an apparent molecular weight in the range of 200. Jolley et al. (1982) found a variety of non-volatile mutagens in a number of chlorinated domestic wastewater effluents which were not susceptible to analysis with conventional methods.

Overall, it must be concluded that the problem associated with disinfection byproducts cannot be confined to concerns for trihalomethanes. Difficulties in analysis of specific compounds make the use of surrogate parameters attractive. Johnson and Jenson (1983) discuss the significance of total organic halides (TOX) as such a surrogate parameter. It is interesting to note that in some cases the trends for formation of TOX may conflict with those for formation of trihalomethanes, thereby resulting in a potential for conflicting goals. For example, Fleischacker and Randtke (1983) observed that TOX decreased with increasing pH in contrast with chloroform which increased with increasing pH.

TREATMENT METHODS FOR TRIHALOMETHANES

General

Several treatment techniques are available for removing trihalomethanes during water treatment. Techniques rely on one of two general approaches: removal of precursor compounds prior to addition of chlorine or the removal of trihalomethanes after chlorine addition. Coagulation and oxidation processes have been used for precursor removal, adsorption processes have been used for both precursor removal and removal of trihalomethanes, and air stripping has been used for the removal of trihalomethanes after their formation.

Coagulation

Coagulation has been shown to be an effective means for removal of a certain portion of the precursor content. As an example, Young and Singer (1979) observed that significant levels of precursors could be removed using the coagulants alum, ferric chloride, and polymer as primary coagulants. Removal was significantly affected by pH with the best results occurring at a slightly acidic pH of 5.5. Batchelor and Yang (1982) found that activated silica enhanced the removal of precursors when using cationic polymer and alum for the water which they were investigating.

To use these types of approaches for removing precursors, the point of prechlorination must be located downstream of the sedimentation basins. In some plants, this may have an undesireable effect with respect to total chlorine contact time across a plant and may result in nuisance problems involving biological growth in those basins upstream of the prechlorination point.

Oxidation

Oxidation is used to alter the structure of the precursor compounds so that products are formed that do not react with chlorine to form trihalomethanes. Use of potassium permanganate has been evaluated by several investigators (Colthurst and Singer, 1982; Voss et al., 1980; Singer et al., 1980) and effectiveness is reported to be a function of raw water quality, pH, and permanganate dose. Singer et al. (1980) reported that permanganate had little effect on chloroform production at dosages typically employed in water treatment and indicated that larger doses would be required to achieve removal of trihalomethane formation potential.

Oxidation has also been reported with ozone and, in some cases, ozone has been supplemented with other agents to catalyze the reaction, including peroxide (Fernandes, 1982) and ultraviolet radiation (Glaze et al., 1982).

Adsorption

Activated carbon is the adsorbent most commonly evaluated for use in control of trihalomethanes. It has been used in both the powdered and the granular form to remove precursors prior to chlorination or to remove trihalomethanes after their formation. Use of powdered activated carbon was evaluated by Epton and Becnel (1981) and was found to be effective only at extremely high dosages for the removal of trihalomethane formation potential. Granular activated carbon can be effective for the removal of both precursors and the trihalomethanes. However, very rapid breakthroughs have been observed to occur in some cases (Englande, 1980 and Symons et al., 1981), thereby raising questions as to the economic feasibility of such an approach. In addition to activated carbon, synthetic resins have been evaluated as a means of adsorption of trihalomethanes (Oulman et al., 1981).

Aeration

Because of the volatile nature of the trihalomethanes, air stripping has been considered as a means of removal. These processes involve either packed towers typical of those used for gas adsorption processes in industry (Kavanaugh and Trussel, 1980) or aerated ponds (EPA, 1983).

ALTERNATIVE DISINFECTANTS

General

To avoid or minimize reactions that form trihalomethanes, several alternatives to breakpoint chlorination can be considered for disinfection in water treatment. The most commonly considered alternative disinfectants are chloramines, chlorine dioxide, and ozone.

Chloramines

Chloramines are formed by the addition of ammonia to react with chlorine. Typically, ammonia is added separately to the process stream either before (pre-ammoniation) or after (post-ammoniation) addition of chlorine to provide a residual disinfectant within the distribution system. Chloramines enjoy an advantage as a residual disinfectant in that they tend to be more stable than free chlorine and persist within a distribution system for a longer period of time.

The order of addition can have an important effect on the types of reactions that occur as illustrated by the fact that pre-ammoniation can prevent the formation of taste and odors that are caused by reactions between chlorine and phenols, whereas postammoniation is generally less effective (NAS, 1980). The order of addition is also important with respect to the formation of trihalomethanes as illustrated by the work of Rice and Bolding (1981). They observed that pre-ammoniation was more effective in preventing the formation of trihalomethanes than was post-ammoniation. In light of these observations, it should be noted that post-ammoniation is the most often used approach (White, 1972).

Although the use of chloramines are observed to result in little formation of trihalomethanes, significant quantities of halogenated organics can be formed during the chloramination process. Specifically, Johnson and Jensen (1983) have expressed concern for the large quantity of TOX that can be formed during chloramination. However, evaluations of specific compounds formed in water treatment as a result of chloramination has been limited (NAS, 1980). In addition to the byproducts, chloramines are toxic in that they directly oxidize hemoglobin leading to methoemoglobin formation and damage red blood cells. Specifically, kidney dialysis patients may be particularly affected by chloramines because they are exposed to much greater blood levels than would be expected in persons exposed to chloramines by ingestion of water (Moore and Calabrese, 1980).

In terms of disinfecting capability, chloramines are generally capable of achieving regulatory criteria for coliforms. In one case, chloramine disinfected water was observed to result in a lower standard plate count than chlorine disinfected water (Norman et al., 1980). However, these observations are not to be interpreted as an indication that chloramine disinfection achieves the desired level of biocidal efficiency for all pathogens. In fact, it has only moderate biocidal activity for bacteria in general and low biocidal activity for both viruses and protazoan cysts (NAS, 1980).

Hoff and Geldreich (1981) indicate that actual performance in the field may differ from those observed in the laboratory. They attribute this potential difference to the manner in which chloramines, are added in the respective settings. Most of the laboratory work has been undertaken using pre-formed chloramines whereas ammonia is typically added after chlorine in the field. This may afford a delay of a few minutes in reaction time required for the formation of chloramines. During this time the free chlorine may achieve a substantial level of kill of pathogenic organisms. Therefore, the method of forming chloramines may have an effect on the degree of disinfection.

The biocidal effectiveness of chloramines is not significantly affected by pH. This contrasts with the observed effect on disinfection with free chlorine where biocidal effectiveness increases with decreased pH (Hoff and Geldreich, 1981).

Chlorine Dioxide

Chlorine dioxide is a compound that is relatively unstable and degrades if stored for an extended period. Therefore, it is typically generated on-site using more stable reactant chemicals that can be stored. The most common approach is to combine sodium chlorite and aqueous chlorine in an acidic solution to yield chlorine dioxide. This reaction normally takes place by passing the reactants through a packed bed reactor that promotes mixing. A contact time of several minutes is generally used.

As an alternative to the above reaction scheme, chlorine dioxide can be formed by acidifying a strong sodium chlorite solution without using clorine as a reactant. Another alternative that is primarily used in large scale industrial applications, such as the paper industry, is the use of sodium chlorate with a reducing agent, sulfur dioxide or methanol. This is more economical at the large scale than using sodium chlorite (NAS, 1980).

Although chlorine dioxide is a chlorinated species, it differs from aqueous chlorine in that oxidation reactions with chlorine dioxide involve a one electron change as compared with the two electron change observed with the hypochlorous acid formed when aqueous chlorine is used. As a consequence, reaction byproducts differ significantly from those observed in conventional breakpoint chlorination. In particular, the formation of appreciable quantities of trihalomethanes is not observed when using chlorine dioxide. In contrast, chlorine is capable of acting through a variety of electrophilic, oxidative, and free radical pathways (Rav-Acha, 1984).

Organic byproducts of concern when using chlorine dioxide include quinones, epoxy, and some chlorinated compounds. The formation of chlorinated species and quinones is related to the ratio of chlorine dioxide to reactive organic matter. At large ratios of greater than 20 to 1, more complete reactions result and the formation of carboxylic acids, ketones, and possibly aldehydes are favored as compared with the formation of the more intermediate species that include the chlorinated products and quinones. However, in water treatment practice, such large ratios are unlikely and the formation of the intermediate products is favored (NAS, 1980).

As in the case of chlorination, it is important to consider the limitations of analytical technique for fully identifying those disinfection byproducts that might be formed when using chlorine dioxide. Zoeteman et al. (1982) reported an increase in direct acting mutagenicity in waters after treatment with chlorine dioxide. Therefore, the extent to which safety may be improved when using chlorine dioxide as opposed to breakpoint chlorination is not certain. However, as pointed out by Rav-Acha (1984), the limited number of reaction pathways available to chlorine dioxide as compared with chlorine suggests that health concerns for organic byproducts would be reduced.

One of the significant concerns with respect to the use of chlorine dioxide is the formation of the inorganic byproducts, chlorite (ClO_2^-) and chlorate (ClO_3^-). These products, in combination with chlorine dioxide, have been shown to result in toxicological effects that are of health concern (Bull, 1982). Because of these concerns, the USEPA has set a recommended maximum contaminant level of 1 mg/l for chlorine dioxide, chlorate, and chlorite, in combination (NAS, 1980). This imposes a constraint on the quantity of primary disinfectant that might be available in the distribution system when using chlorine dioxide. As such, the use of a supplemental disinfectant for such a residual is indicated and secondary disinfection using chloramines has been considered for this purpose (Symons et al., 1981).

Chlorine dioxide has been observed to be an effective disinfectant for bacteria and viruses. Because of a lack of information, one area of uncertainty is its effectiveness for killing protazoan cysts (NAS, 1980) Its overall biocidal effectiveness is influenced by pH, with increase in pH, resulting in improved efficiency (Hoff and Geldreich, 1981).

Ozone

Like chlorine dioxide, ozone is unstable and must be generated on-site. Ozone is commonly formed by contacting oxygen in an air or pure oxygen stream with an electrical corona discharge between two plates. Electrolytic (DuRon, 1982) and UV radiation (Fuller, 1982) methods are also used for generation. The resultant ozone gas must be contacted with the process stream to dissolve the ozone.

Ozone is moderately soluble in water. However, it decomposes relatively rapidly in a reaction that is catalyzed by hydroxide ions which is, therefore, accelerated with increased pH (Hewes and Davison, 1971). Decomposition occurs at a relatively fast rate in both neutral and basic solutions such that an active disinfectant residual cannot be maintained in a distribution system (NAS, 1980).

Reactions associated with ozonation involve either direct reaction with dissolved ozone or reactions with free radical degradation products of ozone. In many cases, the free radicals are much more reactive than ozone itself and these pathways can be especially important in the disinfection of water (Hoigne, 1982). Therefore, a number of reaction pathways are available and a wide range of materials may be oxidized using ozone. As a consequence, ozone can be used as an alternative to chlorine as a primary disinfectant or as a pretreatment oxidant to destroy precursor compounds within a chlorination system.

With ozone, chlorinated byproducts are no longer a significant concern because of the absence of a chlorinated disinfectant. However, concern has been expressed for the possibility of forming expoxides, although none have been found in drinking water, peroxides, and other highly oxidized organic intermediates. One of the problems that is noted in evaluating the byproducts of ozonation is the fact that the ozonation byproducts are either labile or polar in character, thereby rendering them less susceptable to analysis using gas chromotography or combined gas chromotography/mass spectrometry techniques that are common in analysis of organic materials (NAS, 1980).

In an evaluation of the effect of ozonation on Rhine River water, Zoeteman et al., (1982) observed that ozonation tended to reduce mutagenic activity. However, Jolley et al. (1982), in an investigation of disinfection of wastewater effluents, found that ozonation both destroys and produces some non-votatile constituents that show mutagenic activity. Therefore, considerable additional work needs to be performed before the potential for adverse health effects from ozone can be more fully understood.

Ozone is a very strong disinfectant and has excellent biocidal capabilities for bacteria, viruses, and protozoan cysts (NAS, 1980). Unlike chlorine dioxide and free chlorine, its disinfectant capability is not significantly affected by pH within the range of 6 to 9 (Hoff and Geldreich, 1981). However, the ozone residual decays rapidly and cannot be maintained in the distribution system. As with chlorine dioxide, the use of a supplemental disinfectant to maintain a residual is required.

SECTION 5

BACKGROUND

The primary objective of the drinking water industry, and therefore the City of Thornton Utilities Department, is to produce safe, potable water for its consumers at the lowest possible cost. Two factors have a major impact on meeting this objective: raw water quality and degree of treatment. Modifications to Federal regulations change the definition of acceptable water quality. With requirements becoming more stringent, communities with poor raw water quality are forced to look at higher degrees of treatment for their water system.

RAW WATER QUALITY

The City of Thornton, located along the South Platte River downstream of the metropolitan Denver area, has historically experienced quality problems in their raw water supply. The quality of raw water is influenced by more than 90 municipal and industrial wastewater discharges, as well as nonpoint sources of pollution which can include accidental spills of contaminants. The Columbine Water Treatment Plant, which is the largest plant within the system, receives raw water from three primary sources: a series of shallow lakes adjacent to the South Platte River known as Gravel Lakes, shallow wells adjacent to the South Platte River, and lower Clear Creek. The plant is also capable of receiving a limited quantity of raw water from Standley Lake, a higher quality source that receives flow from upper portions of Clear Creek. All three of the primary sources are influenced by the urbanized areas upstream that contribute inorganic and organic contaminants.

In 1978, nitrite (NO_2^-) concentrations approaching 2 mg/L as nitrogen were discovered within the distribution system. Based on data collected by the Thornton laboratory, the source of the nitrite was determined to be ammonia found in high concentrations in the raw water. The ammonia was apparently being oxidized in the distribution system by nitrifying bacteria. This bacterial growth occurred despite the fact that bacteriological standards were being met in the finished water from the Columbine Water Treatment Plant. Because of the acute health effects associated with nitrite, Thornton immediately began a breakpoint chlorination pretreatment process to solve this water quality problem. A raw water source control program was also implemented and led to reductions in the raw water ammonia concentrations.

The breakpoint process predictably resulted in reaction between free chlorine and organic precursors to form higher concentrations of TTHM and TOX. However, because of the acute health concerns of nitrite, Thornton felt that breakpoint chlorination should continue until other long term raw water quality and treatment solutions could be evaluated.

TREATMENT

The Columbine Water Treatment Plant was constructed in 1974. The process flow diagram for this 20 MGD facility is shown in Figure 1. In the treatment process, potassium permangante (0.4 to 0.6 mg/L) is added for iron and manganese removal and ferric chloride (5 to 20 mg/L) is used as the primary coagulant. Chlorine can be added for breakpoint chlorination or predisinfection. Following the addition of the chemicals, the water enters a premix basin having approximately 30 minutes detention time where it is vigorously mixed to promote chemical reactions. Powdered activated carbon is added to the premix basin effluent at dosages of 2 to 4 mg/L for control of taste and odor.

Flocculation and sedimentation are accomplished in basins having a total detention time of approximately 135 minutes. Lime can be added to the clarifier for pH control at dosages up to 20 mg/L. Sludge is withdrawn from the bottom of the clarifiers for disposal.

The settled water is filtered using dual media filters with loading rates of approximately five gallons per minute per square foot. Chlorine is typically added to the filter effluent for postdisinfection to achieve a free residual of approximately 2 mg/L.

The predisinfection process was modified in 1978 to provide breakpoint chlorination for nitrogen removal. Once this immediate water quality problem was solved, evaluation of the breakpoint chlorination process proceeded. Although no specific data were available, there was speculation high concentrations of chlorinated organics could be formed in the breakpoint chlorination process. Initial testing of the water following breakpoint chlorination confirmed this with instantaneous TTHM exceeding 100 ug/L, TTHMFP exceeding 250 ug/L, and instantaneous TOX exceeding 250 ug/L, in the finished water from the Columbine Water Treatment Plant. Further raw water monitoring was necessary to characterize the quality of the raw water. Also, a pilot plant study was recommended to evaluate the effectiveness of existing treatment processes as well as additional processes for treating the available raw water supplies.

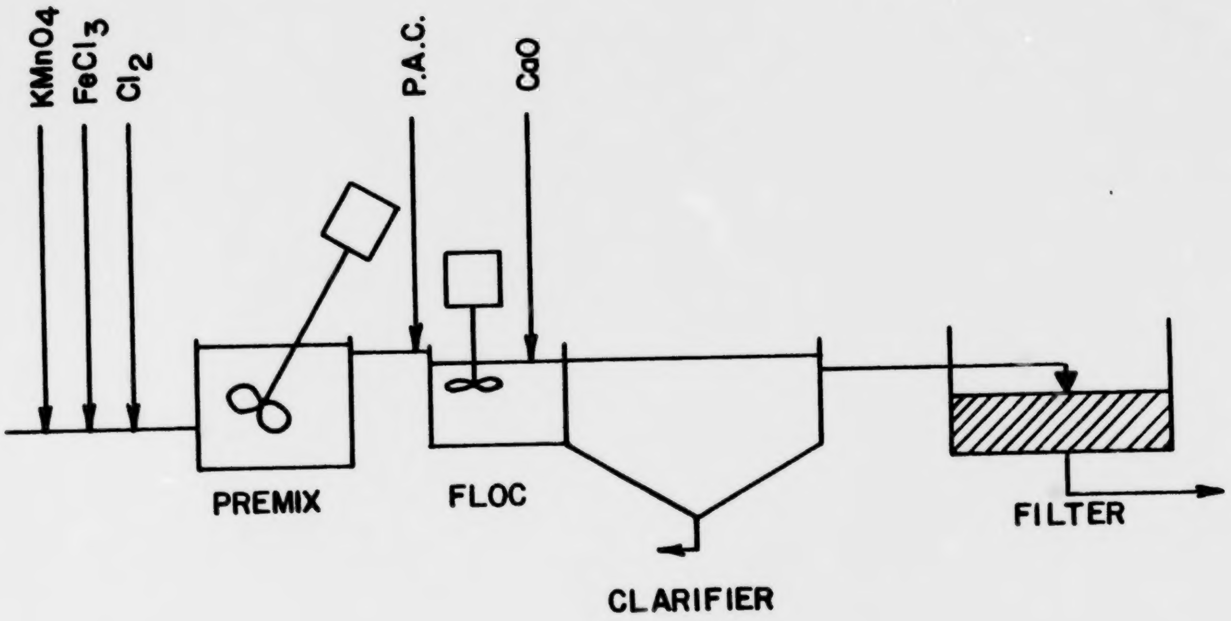

KMnO4
FeCl3
Cl2
P.A.C.
CaO
PREMIX
FLOC
CLARIFIER
FILTER

Figure 1. Columbine Water Treatment Plant processes.

PILOT PLANT PROGRAM

Purpose

The original purpose of the pilot plant program was to evaluate various treatment processes for their ability to treat several raw water sources available to Thornton. All treatment trains included free chlorine disinfection by breakpoint chlorination as one of the processes. The objectives for this original study were to: 1) Evaluate the cost effectiveness and efficiency of existing facilities to treat the various raw water sources. 2) Establish the effects of powdered activated carbon on organic precursor material. 3) Evaluate the practicality of retrofitting the existing rapid sand filters with granular activated carbon. 4) Gain information for selecting an optimum treatment mode for a more in-depth study.

Following the first year of operation, the pilot plant program was changed to include evaluation of alternative disinfectants. This change was implemented because, even though granular activated carbon (GAC) is generally effective in removing organic compounds to a concentration which complies with the TTHM standard of the Safe Drinking Water Act (SDWA), the high cost of GAC and the impracticality of installing GAC within the SDWA compliance schedule made it necessary to evaluate other processes. Several alternative disinfectants were analyzed for inclusion in the study, but only three were selected: 1) chloramines formed by adding ammonia following breakpoint chlorination, 2) chloramines that were pre-formed within the chemical feed streams and injected into the main flowstream, and 3) a combination of pre-formed chloramines and chlorine dioxide.

Process Selection

In 1979, when the City of Thornton began developing the pilot plant program, the first step was to identify processes that should be included to fulfill the purpose of the study. At the time, the purpose of the pilot plant program was to evaluate the effectiveness of certain processes for removal of ammonia and dissolved organics from the water supply. The ammonia concentrations of the raw water have declined during the study period. The reduction appears to be because of management of raw water sources and the influence of the groundwater on the gravel lakes causing either dilution or creating a hydraulic gradient toward the river, thus precluding flow from the river to the gravel lakes.

Ammonia Nitrogen Removal

An evaluation was performed of the four most common treatment processes for nitrogen removal. These processes included: biological nitrogen removal, breakpoint chlorination, ammonia stripping and selective ion exchange.

Although the addition of the high doses of chlorine increase the probability of formation of chlorinated organics, it is felt that breakpoint chlorination is the only practical method of ammonia removal for the Thornton Treatment Plant. This process was being practiced at the full-scale Columbine plant and was incorporated into the pilot plant.

Soluble Organics Removal

Raw water available to Thornton has relatively high concentrations of soluble organics. In addition, the practice of breakpoint chlorination as discussed above will increase the likelihood of formation of chlorinated organics. Several methods of organic removal were investigated including: powdered activated carbon (PAC), granular actiated carbon (GAC), and ozonation. The pilot plant program incorporated an evaluation of the effectiveness of PAC, and because of its proven ability of removing trace organics from water, GAC was selected for evaluation.

Alternative Disinfectants

In 1982, following the first year of pilot plant operation, the study was altered to include evaluations of alternative disinfectants. The disinfectants selected were those that reportedly do not form TTHM. These alternatives included chloramination using two different methods, post ammoniation and pre-formed chlorine solution addition, and chlorine dioxide. Ozone was not selected for study because of equipment costs.

SECTION 6

PILOT PLANT

PROGRAM

Plant Equipment

The pilot plant used for this program was a Neptune-Microfloc, AWT-TR7, rated for a capacity up to 10-gpm. The unit consisted of a raw water rapid-mix chamber, a two-stage flocculation basin, primary settling basin, secondary settling basin, a dual-media filter, and treated water storage chamber. Flow rates through the pilot plant were adjusted by means of a flow meter mounted on the raw water influent line. A schematic of the plant is included in Figure 2. Treatment chemicals could be added to any of the plant processes in order to allow for complete flexibility of points of application.

Carbon columns used during the pilot program consisted of four, 6-inch-diameter, 8-foot-tall, glass columns with sample taps at six locations for monitoring organic breakthrough. Each column had 5.5 feet of Westvaco Nuchar HG 40, 12x40 mesh, coal-base granular activated carbon (GAC) as media. The carbon was selected from bench scale laboratory tests on GAC that was provided by several manufacturers. The columns could be operated in series or in parallel, with treated water from the pilot plant pumped through the columns.

Plant Operation

The retention time and loading rates of the pilot plant best resembled the full-scale Columbine Treatment Plant when operated at a flow rate of 6 gpm. This was selected as the standard treatment rate for the program and resulted in the following loading rates for the various unit processes:

- Flash Mixer:
  - Hydraulic detention time = 1.7 min.
- Flocculation:
  - Chamber 1 (downflow)
    - Hydraulic detention time = 18 min.
  - Chamber 2 (upflow)
    - Hydraulic detention time = 18 min.

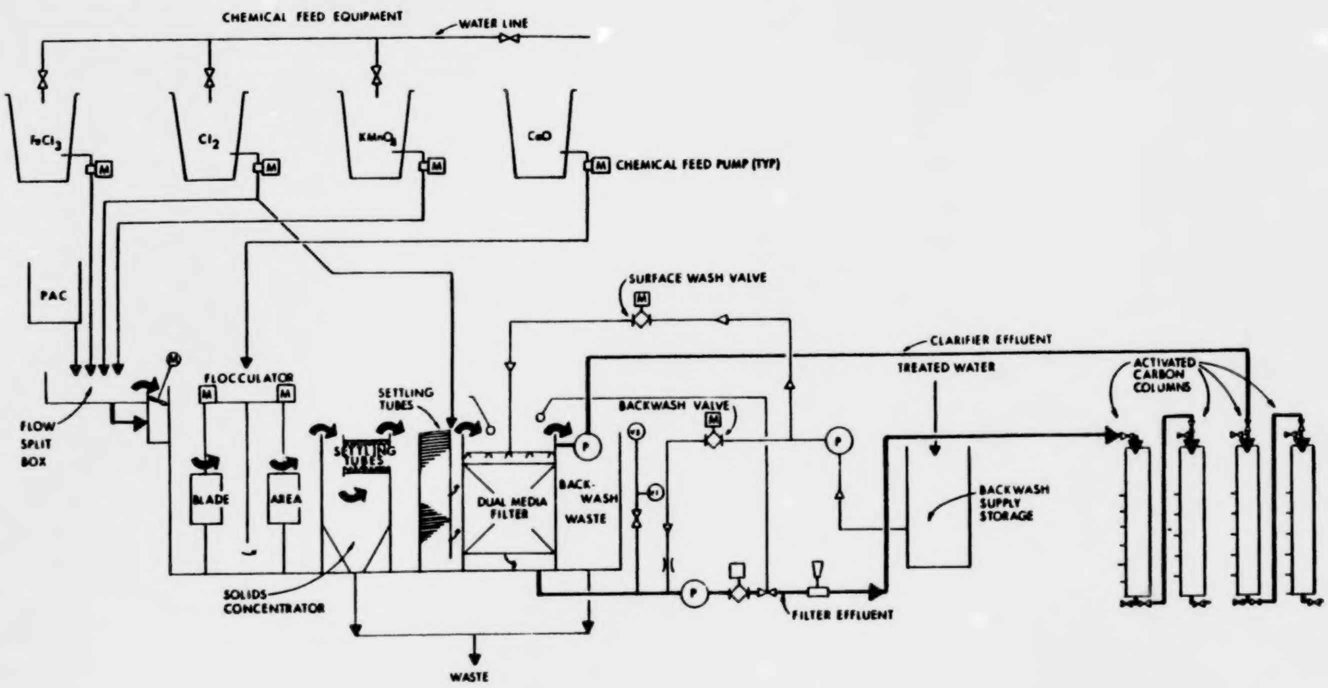

CHEMICAL FEED EQUIPMENT
WATER LINE
$FeCl_3$
Cl_2
$KMnO_4$
CaO
M
CHEMICAL FEED PUMP (TYP)
PAC
FLOW SPLIT BOX
FLOCCULATOR
BLADE
AREA
SETTLING TUBES
SETTLING TUBES
SOLIDS CONCENTRATOR
DUAL MEDIA FILTER
BACK-WASH WASTE
WASTE
SURFACE WASH VALVE
BACKWASH VALVE
P
FILTER EFFLUENT
CLARIFIER EFFLUENT
TREATED WATER
BACKWASH SUPPLY STORAGE
ACTIVATED CARBON COLUMNS

Figure 2. Pilot plant processes.

Both chambers were equipped with variable speed vertical flocculation paddles with a maximum tip velocity of 2.5 fps.

- Clarification:

  Clarifier 1 (with 60° inclined settling tubes).
  Tube loading rate = 1 gpm/ft^2.

  Clarifier 2 (with 7-1/2° inclined settling tubes).
  Tube loading rate = 0.80 gpm/ft^2.

- Filtration:

  Surface Loading Rate = 2 gpm/ft^2

- GAC:

  (Two columns operated in series of a flow rate of 1 gpm.)

  Surface Loading Rate = 5 gpm/ft^2

  Empty Bed Contact Time (per column) = 8 minutes
  Empty Bed Contact Time (per pair of columns) = 16 minutes

Modes of Operation

The Thornton Pilot Plant Program was divided into six operational modes. In general, each mode represented a refinement of the previous mode and/or an additional area of interest to be investigated. The modes of operation are shown schematically in Figure 3. Below are descriptions of each of the six modes.

Mode 1

The Mode 1 configuration of the Thornton Pilot Plant was identical to the full-scale Columbine Treatment Plant with the exception of the addition of granular activated carbon columns. Under this mode, chlorine was added in the premix basin to achieve breakpoint chlorination. The purpose of this mode was to determine the extent to which the Pilot Plant performance simulated that of the full-scale facility.

Mode 2

The Mode 2 configuration of the Pilot Plant was identical to Mode 1 except that the location of breakpoint chlorination was moved downstream from the premix basin to the clarifier effluent. The purpose of this modification was to maximize the removal of precursor material prior to the addition of chlorine, thus reducing the formation of chlorinated organics. The initial

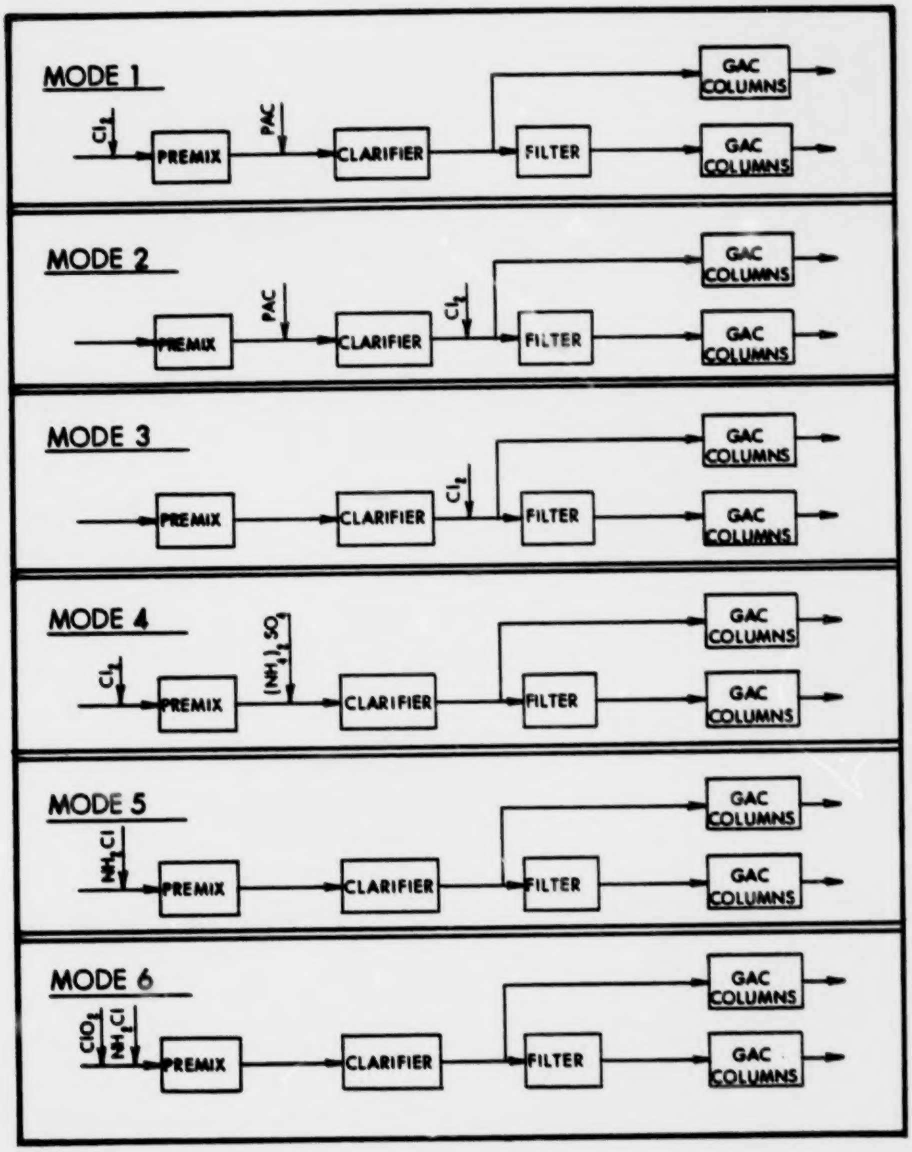

MODE 1
Cl_2
PREMIX
PAC
CLARIFIER
FILTER
GAC COLUMNS
GAC COLUMNS
MODE 2
PREMIX
PAC
CLARIFIER
Cl_2
FILTER
GAC COLUMNS
GAC COLUMNS
MODE 3
PREMIX
CLARIFIER
Cl_2
FILTER
GAC COLUMNS
GAC COLUMNS
MODE 4
Cl_2
PREMIX
$(NH_4)_2SO_4$
CLARIFIER
FILTER
GAC COLUMNS
GAC COLUMNS
MODE 5
NH_2Cl
PREMIX
CLARIFIER
FILTER
GAC COLUMNS
GAC COLUMNS
MODE 6
ClO_2
NH_2Cl
PREMIX
CLARIFIER
FILTER
GAC COLUMNS
GAC COLUMNS

Figure 3. Pilot plant modes of operation.

results of this mode showed that it was impractical to treat the raw water without some form of disinfection at the head of the plant. Excessive biological slime growths occurred almost immediately and required control. As a result, small amounts of chlorine were added to the raw water in quantities sufficient to form chloramines. This minimal prechlorination prevented the formation of slime while allowing for the removal of some precursor material.

Mode 3

The Mode 3 configuration was identical to Mode 2 with the exception that the addition of powdered activated carbon was eliminated from the process. The purpose of this mode was to provide a basis of comparison to evaluate the effectiveness of powdered activated carbon on the removal of organic precursor material.

Mode 4

Mode 4 consisted of breakpoint chlorination in the premix basin followed immediately by the addition of ammonium sulfate to form chloramines. Breakpoint chlorination, followed by rapid conversion to chloramines through the addition of ammonium sulfate, could possibly reduce the time that free chlorine is available for formation of trihalomethane and other chlorinated organics.

Mode 5

The Mode 5 configuration consisted of the addition of a solution of chloramines that were formed off-line prior to their introduction into the main flowstream. The purpose of this mode was to eliminate the possibility of formation of chlorinated organics with free chlorine that exists in the flow stream just prior to ammoniation under the Mode 4 scheme.

Mode 6

Mode 6 consisted of a "dual disinfection" system using both chlorine dioxide and chloramines, with addition at the inflow to the plant. The purpose of this mode was to gain the superior disinfecting capabilities with chlorine dioxide and the persistence of the chloramines for maintaining a residual throughout the distribution system, while avoiding the formation of trihalomethanes. Concerns for Mode 6 included the need to control the chlorite, chlorate, and chlorine dioxide concentrations such that an adverse health effect is not experienced. GAC columns were only operated during the early period of this mode of operation since results from the previous modes provided adequate data for evaluation of GAC performance.

Analytical Program

Sampling

The sample points selected for the pilot plant program are listed in Table 1 and are shown schematically in Figures 4 and 5. These figures illustrate the process train used in the pilot plant and full-scale treatment plant, respectively.

The sample point for full scale raw blend was selected so a determination could be made of the quality of raw water being received at both the full scale and pilot plants. Throughout the various modes of operation, the raw water sources changed, requiring ongoing monitoring of the raw blend. The premix effluent, clarifier effluent, and filter effluent were selected as locations for monitoring the effect of different unit processes on water quality. By sampling the effluent of each of the processes, the changes in water quality across the process could be monitored to determine the effectiveness of each process during each mode of operation.

Process water from both the clarifier effluent and filter effluent were respectively treated in the pilot granular activated carbon columns to examine the effect of granular activated carbon on removal of organic precursors and chlorination byproducts under two levels of treatment of the column inflow. Carbon columns numbers 9 and 10 were used to treat pilot plant clarifier effluent, while columns numbers 11 and 12 were used to treat pilot plant filter effluent. The former columns were intended to resemble a filter retrofit application in which filter media is replaced with granular activated carbon, while the latter columns simulate a granular activated carbon process installed following filtration.

Analyses

The sampling schedule, along with the parameters analyzed in both the full scale and pilot plant processes, is shown in Table 2. Procedures used for the collection, preservation, and storage of the samples are shown in Table 3. A Quality Assurance (QA) Project Plan, used to ensure accuracy in sampling and analytical procedures, was prepared in September, 1981 and approved by the EPA for use during the pilot plant program. This QA Plan addressed the use of proper sampling containers, proper sampling technique, preservation and storage of samples, and methods to be used in the analyses of organic, inorganic, and microbiological parameters. At the request of the EPA, a QA audit was conducted in May, 1982, on the pilot plant program by S-CUBED, a consulting firm specializing in this area. The report concluded that a very high level of QA was found at the Thornton analytical laboratory with the people adhering closely to the QA activities contained in an excellent plan.

TABLE 1. FULL SCALE AND PILOT PLANT SAMPLE POINTS

Designation	No.	Name	Description
FSRB	1	Full Scale Raw Blend	Sampled at Columbine WTP raw water lines at the sample pump located in pipe gallery.
FSPE	2	Full Scale Premix Effluent	Sampled at Columbine WTP premix basin effluent as the water comes over the premix weirs.
PPPE	3	Pilot Plant Premix Effluent	Sampled at sample line from pilot plant premix using a siphon.
FSCE	4	Full Scale Clarifier Effluent	Sampled at Columbine WTP clarifier effluent as the water comes over the weirs before post chlorination.
PPCE	5	Pilot Plant Clarifier Effluent	Sampled at pilot plant clarifier as the water comes over the weir, before post chlorination.
FSFE	6	Full Scale Filter Effluent	Sampled at Columbine WTP effluent as the water enters the Clearwell.
PPFE	7	Pilot Plant Filter Effluent	Sampled at pilot plant filter effluent as the water enters the Clearwell.
FSAD	8	Full Scale Actual Distribution System	Sampled from a point near the outer extremity of the distribution system still having a chlorine residual to reflect maximum residence time in system. Actual location was 12025 Grant Street. The estimated residence time under normal flow conditions determined by a tracer study was 5 days.

(continued)

TABLE 1. (continued)

Designation	No.	Name	Description
CC 9-6	9	Carbon Column No. 9 Effluent	First in series downstream of Pilot Plant Filter Effluent
CC 10-6	10	Carbon Column No. 10 Effluent	Second in series downstream of Pilot Plant Filter Effluent
CC 11-6	11	Carbon Column No. 11 Effluent	First in series downstream of Pilot Plant Clarifier Effluent
CC 12-6	12	Carbon Column No. 12 Effluent	Second in series downstream of Pilot Plant Clarifier Effluent

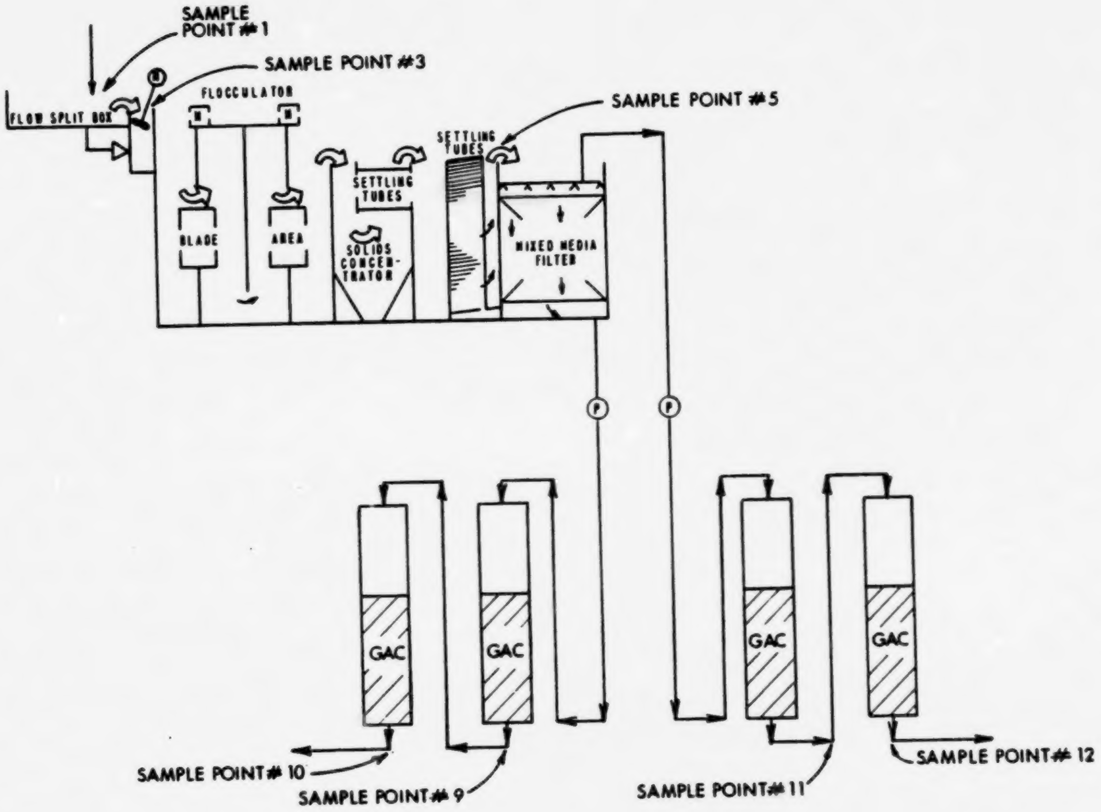

SAMPLE POINT #1
SAMPLE POINT #3
M
FLOCCULATOR
FLOW SPLIT BOX
M
M
SAMPLE POINT #5
SETTLING TUBES
SETTLING TUBES
BLADE
AREA
SOLIDS CONCENTRATOR
MIXED MEDIA FILTER
P
P
GAC
GAC
GAC
GAC
SAMPLE POINT# 10
SAMPLE POINT# 9
SAMPLE POINT# 11
SAMPLE POINT# 12

Figure 4. Pilot plant sample points.

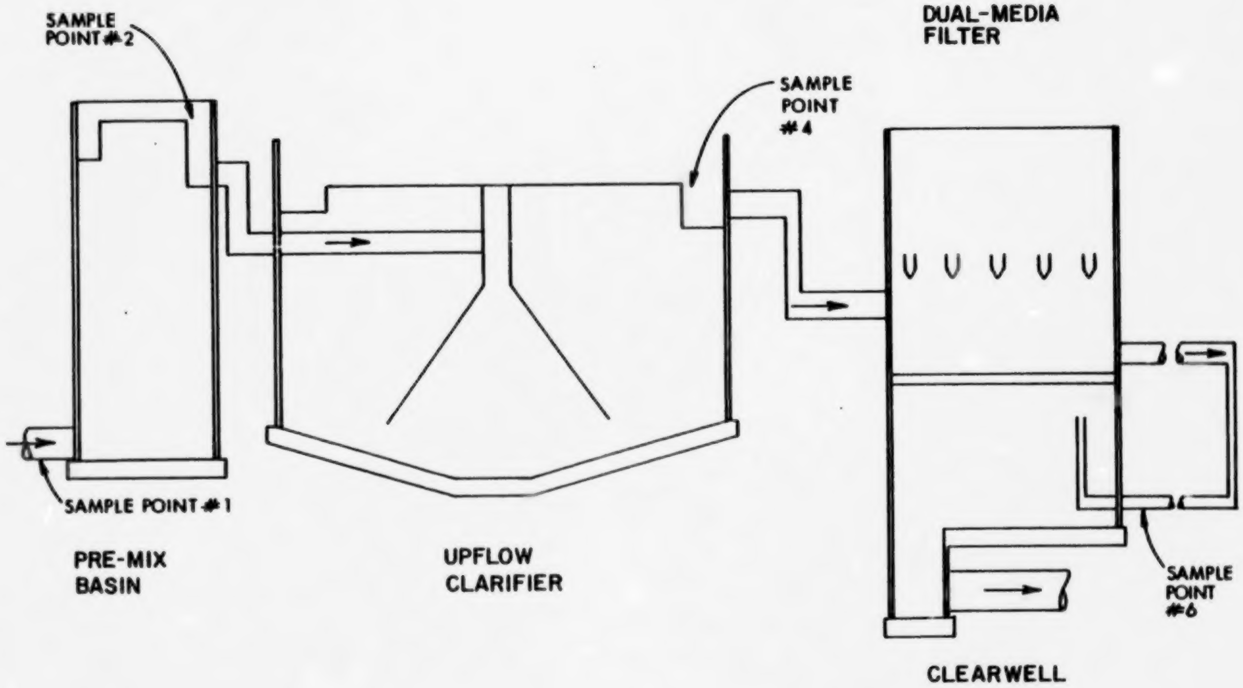

SAMPLE POINT #2
DUAL-MEDIA FILTER
SAMPLE POINT #4
SAMPLE POINT #1
PRE-MIX BASIN
UPFLOW CLARIFIER
SAMPLE POINT #6
CLEARWELL

Figure 5. Columbine Water Treatment Plant sample points.

TABLE 2. FULL SCALE AND PILOT PLANT SAMPLING SCHEDULE

Location	I-TTHM	TTHM-FP (B)	TTHM-FP (C)	I-TOX	TOX-FP (B)	TOC	Metals	SPC & Coliphage	Total Coliform	TKN	NH_3	NO_3	NO_2	DO
1. FS RB	1/wk	1/wk	1/wk	1/2wk	1/2wk	1/2wk	1/qtr	2/wk	1/wk	1/2wk	1/wk	1/wk	1/wk	2/wk
2. FS PE														
3. PP PE														
4. FS CE	1/wk	1/wk									1/wk	1/wk	1/wk	
5. PP CE	1/wk	1/wk						2/wk			1/wk	1/wk	1/wk	2/wk
6. FS PE	1/wk	1/wk	1/wk	1/2wk	1/2wk	1/2wk	1/qtr	2/wk	1/wk	1/2wk	1/wk	1/wk	1/wk	2/wk
7. PP PE	1/wk	1/wk	1/wk	1/2wk	1/2wk	1/2wk	1/qtr	2/wk	1/wk	1/2wk	1/wk	1/wk	1/wk	2/wk
8. FS AD	1/wk			1/2wk		1/2wk	1/yr	1/wk	1/wk	1/mo	1/mo	1/mo	1/mo	
9. CC 9-6	1/wk	1/wk	1/wk			1/2wk								
10.CC 10-6	1/wk	1/wk	1/wk	1/2wk	1/2wk	1/2wk	1/qtr	2/wk	1/wk					2/wk
11.CC 11-6	1/wk	1/wk	1/wk			1/2wk								
12.CC 12-6	1/wk	1/wk	1/wk	1/2wk	1/2wk	1/2wk	1/qtr	2/wk	1/wk					2/wk

NOTES:

1. TOX, TOC & TKN samples were collected during the same week.
2. The FS AD sample for TKN, NH_3, NO_3, and NO_3 was collected at the same time as TOX, TOC and TKN samples.
3. The pH, Temp. and Cl_2 analyses to be performed along with all THM & TOX analyses, also ClO_2, ClO_2 and ClO_3 analyses were performed on PPCE, PPFE, CC9-6, CC10-6, CC11-6 and CC12-6.
4. TTHM-FP analyses were conducted using two different chlorine dosage schedules. Schedule B = Total Chlorine residual of 2 mg/L greater than demand and Schedule C = 10 mg/L greater than demand. TOX-FP analyses for Schedule B only.

TABLE 3. COLLECTION, PRESERVATION AND STORAGE OF WATER SAMPLES

DETERMINATION	CONTAINER	MINIMUM SAMPLE SIZE	PRESERVATION	MAXIMUM HOLDING PERIOD
Alkalinity	plastic or pyrex bottle, tightly sealed, no bubbles	100 ml	cool to 4^oC	14 days
Arsenic	plastic or glass HNO_3 rinse	100-200 ml	HNO_3 to pH<2	6 months
Barium	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH<2	6 months
Cadmium	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH<2	6 months
Chlorine (residual)	glass	200-500 ml	determine on site	analyze immediately
Chromium	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH<2	6 months
Coliform (fecal or total)	sterile plastic or glass	100-1000 ml	cool to 4^oC .008% w/v $Na_2S_2O_3$	6 hours
Coliphage	sterile plastic or glass	100-1000 ml	cool to 4^oC .008% w/v $Na_2S_2O_3$	6 hours
Copper	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH <2	6 months
Hardness	plastic or glass	50-100 ml	HNO_3 to pH <2	6 months
Iron (total)	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH <2	6 months
Manganese	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH <2	6 months

(continued)

TABLE 3. (continued)

DETERMINATION	CONTAINER	MINIMUM SAMPLE SIZE	PRESERVATION	MAXIMUM HOLDING PERIOD
Mercury	plastic or glass HNO_3 rinse	500 ml	HNO_3 to pH <2 .05% w/v $K_2Cr_2O_7$	28 days
Nitrogen (Ammonia)	plastic or glass	1000 ml	H_2SO_4 to pH <2 cool to 4°C	28 days
Nitrogen (Nitrate)	plastic or glass	100-250 ml	cool to 4°C	48 hours
Nitrogen (Nitrate/Nitrite)	plastic or glass	100-250 ml	H_2SO_4 to pH <2 cool to 4°C	28 days
Nitrogen (Nitrite)	plastic or glass	100-250 ml	cool to 4°C	48 days
Nitrogen (Total Kjeldahl)	plastic or glass	500 ml	H_2SO_4 to pH <2 cool to 4°C	28 days
Organic Carbon	amber glass TFE liner	60 ml	H_2SO_4 to pH <2 cool to 4°C	28 days
Organohalides	amber glass TFE liner	125 ml	.012% w/v Na_2SO_3 no headspace	14 days
Organohalide (formation potential)	amber glass TFE liner	125 ml	10 ppm free Cl^- residual, stored 5 days at pH 7.8, dechlorinated with Na_2SO_3	14 days
Oxygen, Dissolved	plastic or glass	300 ml	determine on site	analyze immediately
Orthophosphate	plastic or glass	100 ml	filter immediately cool to 4°C	48 hours
Phosphorous (Total)	plastic or glass	100 ml	H_2SO_4 to pH <2 cool to 4°C	28 days

(continued)

TABLE 3. (continued)

DETERMINATION	CONTAINER	MINIMUM SAMPLE SIZE	PRESERVATION	MAXIMUM HOLDING PERIOD
pH	plastic or glass	100 ml	none	analyze immediately
Residue (Total Filterable)	plastic or glass	100 ml	cool to 4^{o}C	7 days
Selenium	plastic or glass HNO_3 rinse	200-500 ml	HNO_3 to pH <2	6 months
Silver	plastic HNO_3 rinse	200-300 ml	HNO_3 to pH <2	30 days
Standard Plate Count	sterile plastic or glass	100-1000 ml	cool to 4^{o}C .008% w/v $Na_2S_2O_3$	6 days
Trihalomethanes	glass, TFE liner	40 ml	.012% w/v Na_2SO_3 no headspace	7 days before extraction
Trihalomethanes (formation potential)	glass, TFE liner	40 ml	10 ppm free Cl^- residual, stored 5 days at pH 7.8, dechlorinated with Na_2SO_3	7 days before extraction
Turbidity	plastic or glass	100 ml	cool to 4^{o}C	48 hours
Zinc	plastic or glass	200-500 ml	HNO_3 to pH <2	6 months

Following is a brief description of the parameters analyzed during the pilot plant study. Listings of the procedures and instrumentation used are presented in Tables 4 and 5, respectively.

Inorganic. Selected pilot plant and full scale samples were analyzed for alkalinity, chlorine residual, hardness, iron, manganese, nitrogen species, dissolved oxygen, and pH. The analyses for alkalinity and hardness were ended in September, 1983. These parameters are typically monitored in a water treatment plant, but were not significant to the pilot plant program other than for operational control and general characterization of the water quality. Iron and manganese analyses were performed only from June 23, 1982 through October 6, 1982. The analyses for both free and total chlorine residual were performed to monitor the effect of chlorine on other parameters. The nitrogen species that were determined included total Kjeldahl nitrogen (TKN), ammonia, nitrate, and nitrite.

Physical. Temperature was determined on all pilot plant and full scale samples throughout the program so that the effect of temperature on other parameters could be evaluated. Selected samples were analyzed for turbidity through September, 1983 when this analysis was terminated.

Organic. The pilot plant and full scale samples were analyzed for total organic carbon (TOC), trihalomethane (TTHM), and total organic halogen (TOX). TOC serves as an indicator of the overall organic content of the water. TTHM and TOX, respectively, indicate the specific and general chlorination byproducts formed during the treatment process. In addition, analyses were performed for trihalomethane formation potential (TTHMFP) and total organic halogen formation potential (TOXFP). These parameters indicate the potential for formation of TTHM and TOX and were determined by exposing samples to a free chlorine residual held over a 5-day period at ambient water temperature. These analyses were performed using various chlorine dosages. The formation potential data in this report are for schedules B and C which represent chlorine dosages of 2 and 10 mg/L over the one hour chlorine demand, respectively. A discussion of critical parameters in the analyses for formation of TTHM and TOX is included in Appendix A.

Beginning in January, 1985, analyses were performed for dichloroacetonitrile and chloropicrin on a routine basis. Previously, some analytical work had been conducted on these compounds by Old Dominion University.

Microbiological. Total coliform, standard plate count, and coliphage analyses were conducted on samples from the pilot plant and the full-scale plant. Total coliform is the parameter

TABLE 4. ANALYTICAL PROCEDURES

Inoganic Methods		
Alkalinity	403[c]	Acid Titration
Chlorine Residual	330.4[a]	Titrimetric, DPD-FAS
Hardness	130.2[a]	Titrimetric, EDTA
Heavy Metals		
Arsenic	206.2[a]	Furnace Technique
Barium	208.2[a]	Furnace Technique
Cadmium	213.2[a]	Furnace Technique
Chromium	218.2[a]	Furnace Technique
Copper	220.2[a]	Furnace Technique
Iron	236.2[a]	Furnace Technique
Lead	239.2[a]	Furnace Technique
Manganese	243.2[a]	Furnace Technique
Mercury	245.1[a]	Manual Cold Vapor
Selenium	270.2[a]	Furnace Technique
Silver	272.2[a]	Furnace Technique
Zinc	289.2[a]	Furnace Technique
Ammonia-Nitrogen	350.1[a]	Colorimetric, Automated Phenate
Kjeldahl-Nitrogen	351.2[a]	Colorimetric, Semi-Automated Block Digester, AAII
Nitrate+Nitrite-Nitrogen	353.2[a]	Colorimetric, Automated Cadmium Reduction
Oxygen-Dissolved	360.2[a]	Modified Winkler, Full-Bottle Technique
pH	150.1[a]	Electrometric
Orthophosphate	365.2[a]	Colorimetric, Ascorbic Acid, Single Reagent
Phosphorus-Total	365.4[a]	Colorimetric, Semi-Automated Block Digester, AAII

(continued)

TABLE 4. (continued)

Organic Methods		
Total Organic Carbon	415.1[a]	Combustion or Oxidation
Total Organic Halide	450.1[a]	Microcoulmetric-Titration
Trihalomethane	501.2[b]	Liquid/Liquid Extraction
Physcial Methods		
Residue, Filterable	160.1[a]	Gravimetric, 180°C
Temperature	170.1[a]	Thermometric
Turbidity	180.1[a]	Nephalometric
Microbiological Methods		
Fecal Coliform	909 C[c]	Fecal Coliform Membrane Filter Procedure
Total Coliform	909 A[c]	Total Coliform Membrane Filter Procedure
Standard Plate Count	907 A[c]	Pour Plate Method
Coliphage	919 C[d]	Single Media Layer Plate Count

a - E.P.A. "Methods for Chemical Analysis of Water and Wastes" E.P.A. - 600/4-79-020

b - Federal Register, December 3, 1979

c - *Standard Methods for the Examination of Water and Wastewater, 15th Edition*, 1981.

d - Modified two layer procedure as presented by Mark Adams.

TABLE 5. INSTRUMENTATION

Atomic Absorption Spectrophotometer
Instrumentation Laboratories 651
(with 555 flameless atomizer)
254 Fastac Auto Sampler

Automatic Analyzer
Technicon AutoAnalyzer II

Balance
Mettler H33 analytical balance
Mettler PR1200 top load balance

Gas Chromatograph
Hewlett Packard 5880A
7672 A Automatic Sampler

Specific Ion Meter
Orion 901
Orion 701
Orion 407A portable

Spectrophotometer
Bausch & Lomb Spectromic 710

Total Organic Carbon Analyzer
Dohrmann Envirotech
DC 54 Ultra Low Organics Module

Total Organic Halide Analyzer
Dohrmann Envirotech
DX 20 total organic halide analyzer

Turbidimeter
Hach 2100 A

typically used to indicate bacteriological quality and is the parameter regulated by the drinking water standards. Standard plate count gives a more sensitive indication of the overall bacteriological quality. Analysis for coliphage began during August, 1984. The techniques for the analysis were still being developed by the Thornton staff during the pilot plant study, so no results are presented. Coliphage is presently being examined by EPA as an indicator for enteric viruses. Research is still being performed on the various strains and growth media to allow correlation of coliphage to viruses. Recent research has indicated a lack of comparability of disinfection resistance between the polio virus and the F_2 coliphage.

RESULTS

The results presented below show the correlation between the pilot plant and the full-scale Columbine Water Treatment Plant, the ability of a process or a process train to remove specific constituents, the difference in formation of chlorinated organics in using alternative disinfection techniques, and the difference in bacteriological quality resulting from use of the alternative disinfectants.

Pilot Plant Correlation

An important part of the pilot plant program was to determine if the pilot plant results are representative of full-scale operation. If the pilot plant is representative, the data can be used to predict full-scale results. During the period between June 23, 1982 and September 2, 1982, the pilot plant was operated in Mode 1 and the full-scale Colmbine Water Treatment Plant was also in operation. Since the pilot plant was operated in Mode 1 to resemble the full-scale Columbine Water Treatment Plant, the data from this period was used to determine if the performance of the pilot plant correlated to the performance of the full-scale plant. Data are compared for the full-scale filter effluent and the pilot plant filter effluent. Data plotted for TOC, instantaneous TTHM, TTHMFP, instantaneous TOX, and TOXFP are included in Figures 6 through 11. Each of these analyses shows a good correlation between the performance of the full-scale plant and the pilot plant. Therefore, it is presumed that data from other modes of operation represent what would occur at full-scale.

Process Evaluation

The results from TOC, TTHM, and TOX analyses are presented to show the effectiveness of the processes and process trains in removing these constituents. Both instantaneous and terminal data are presented for the TTHM and TOX. Since procedures for chlorine dose control in the terminal analyses were modified during the pilot plant study, only the comparable data are used.

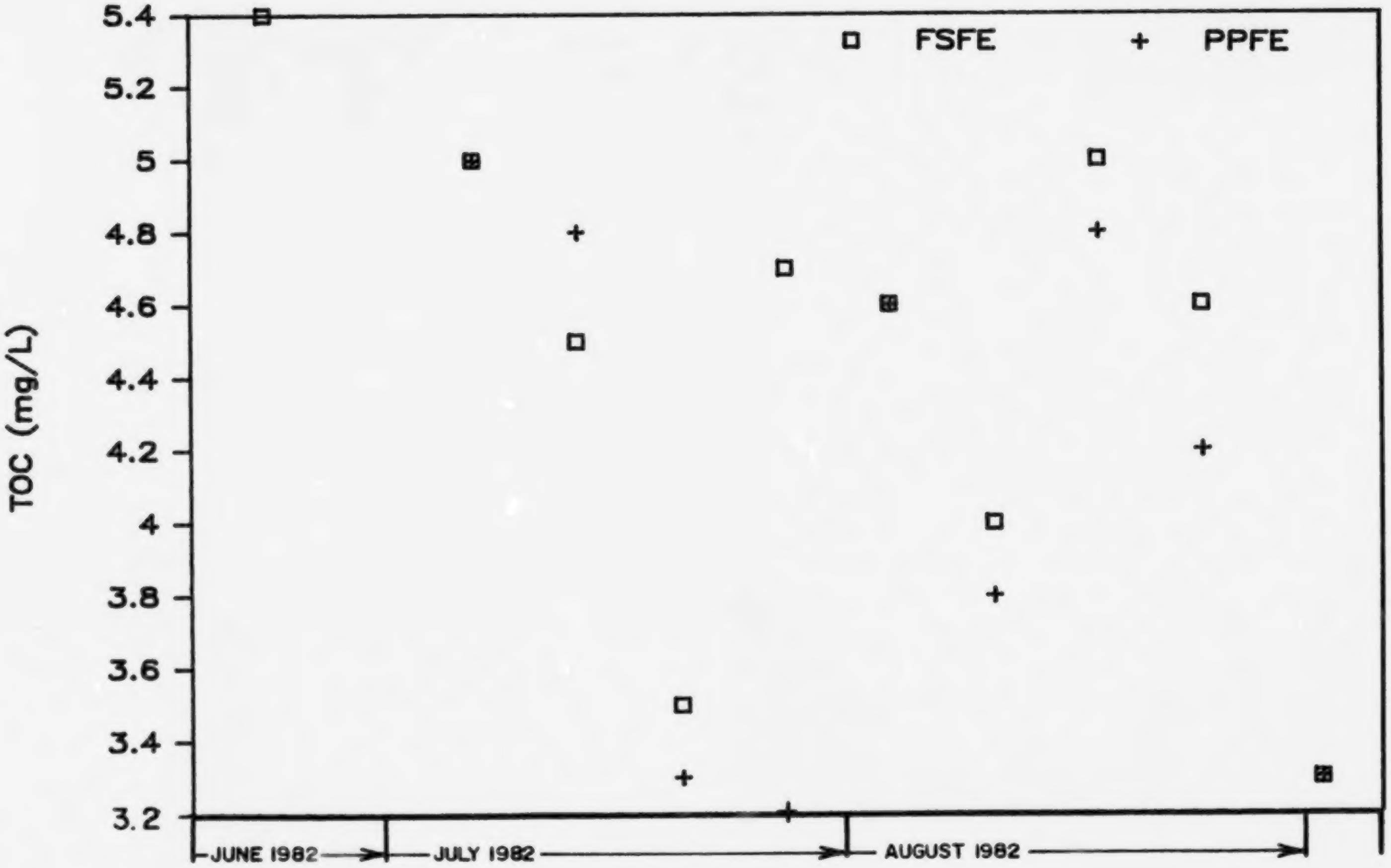


Figure 6. Performance comparison of pilot plant versus full-scale operation in regard to TOC.

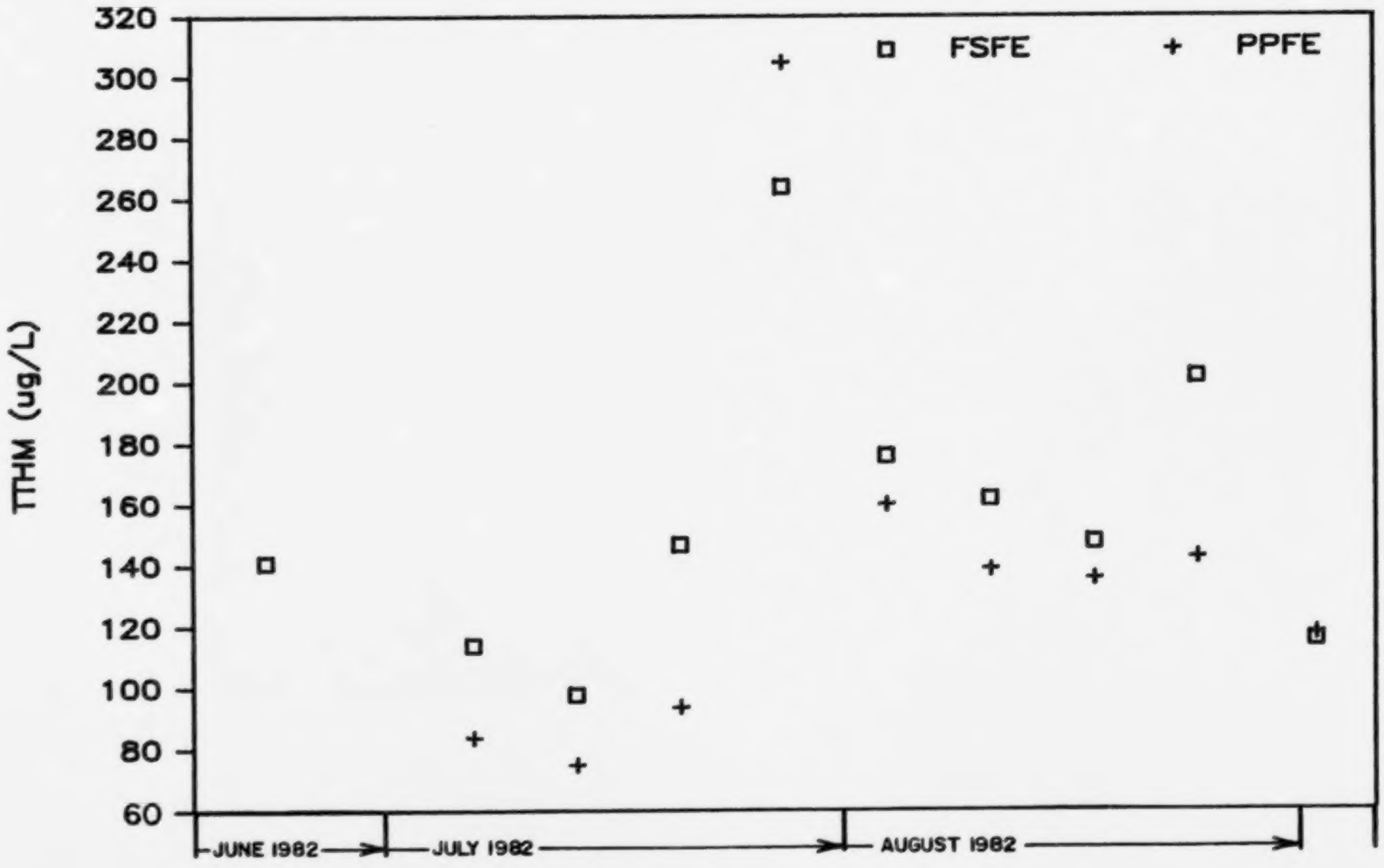


Figure 7. Performance comparison of pilot plant versus full-scale operation in regard to TTHM.

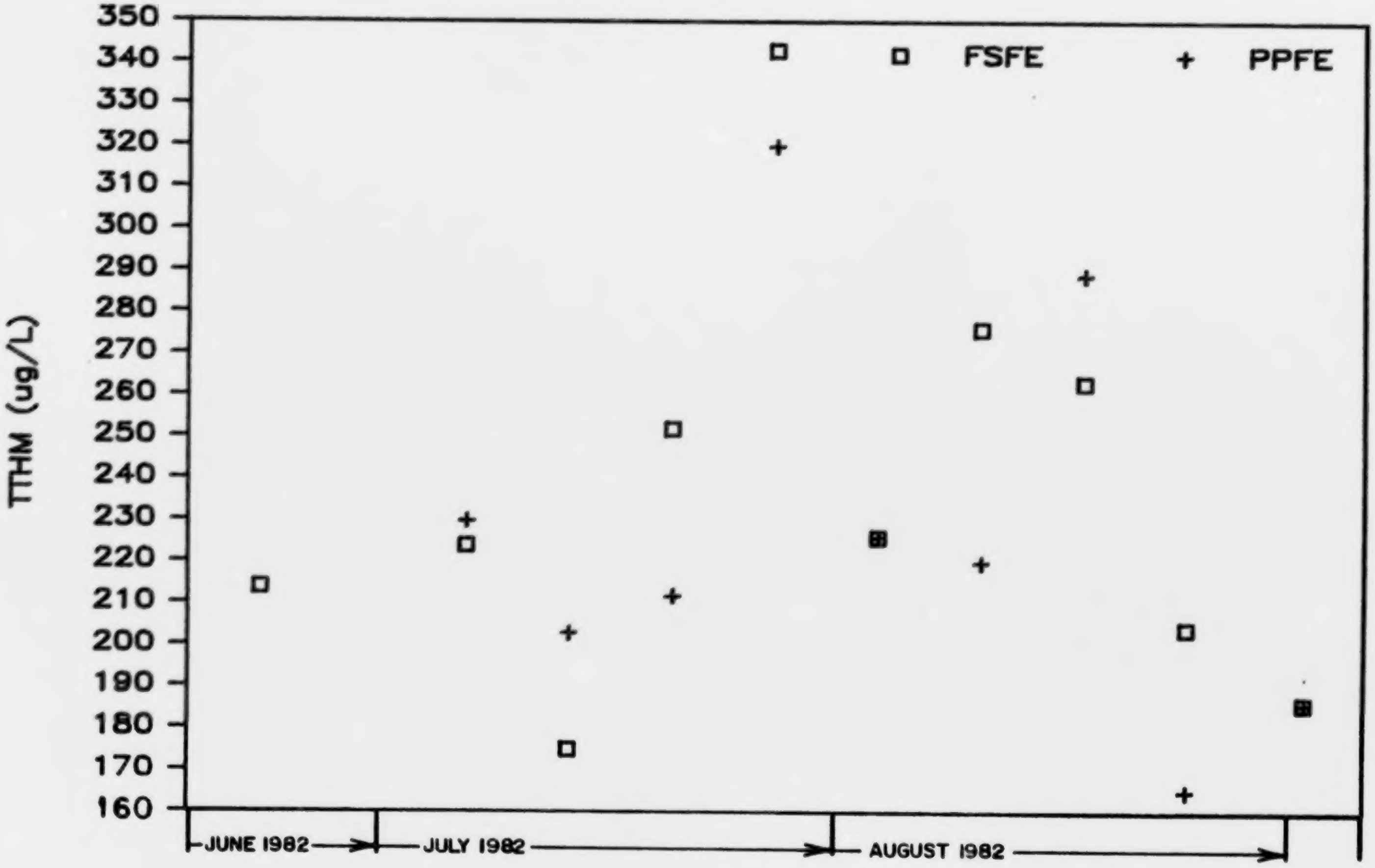


Figure 8. Performance comparison of pilot plant versus full-scale operation in regard to terminal TTHM.

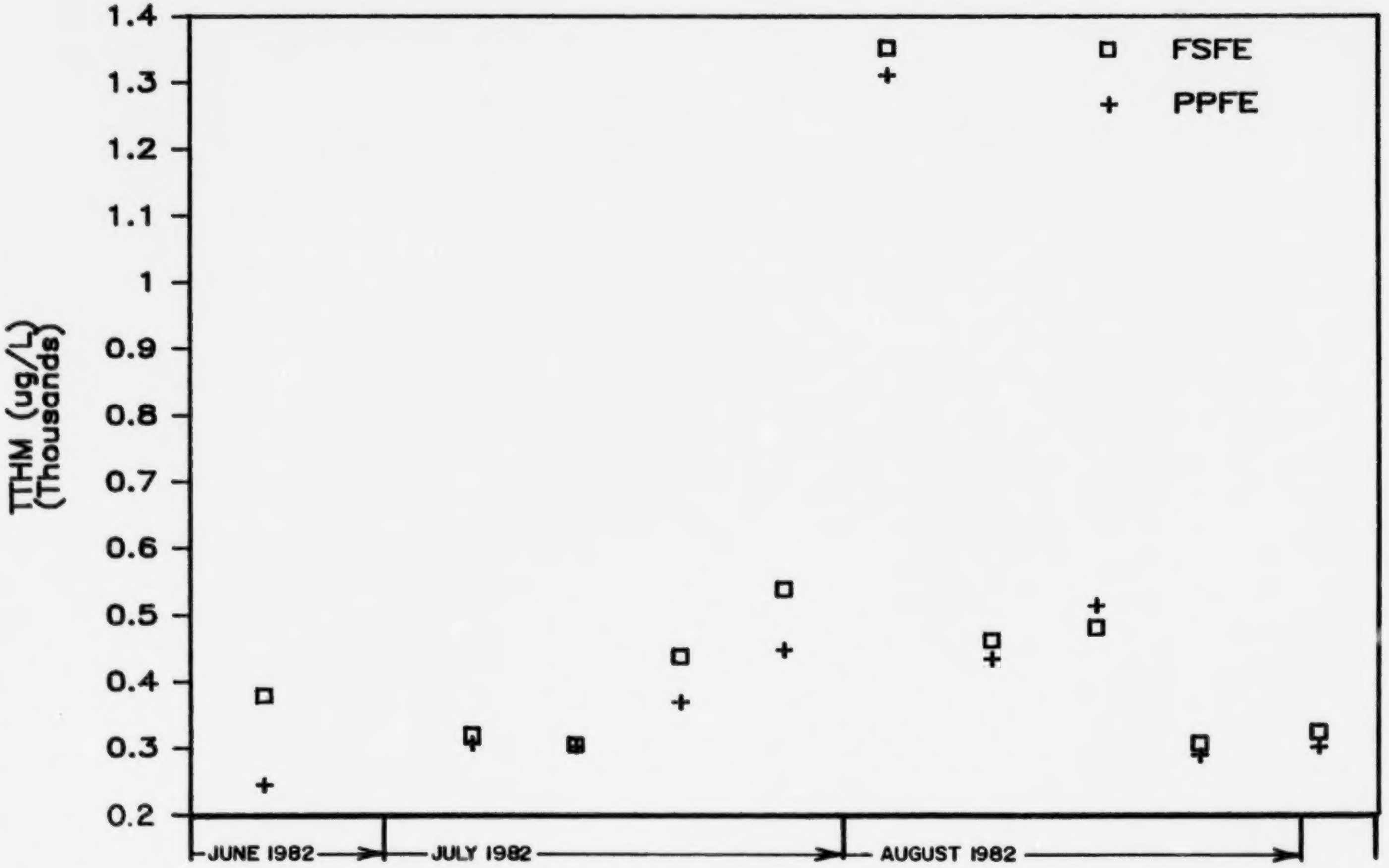


Figure 9. Performance comparison of pilot plant versus full-scale operation in regard to TTHMFP.

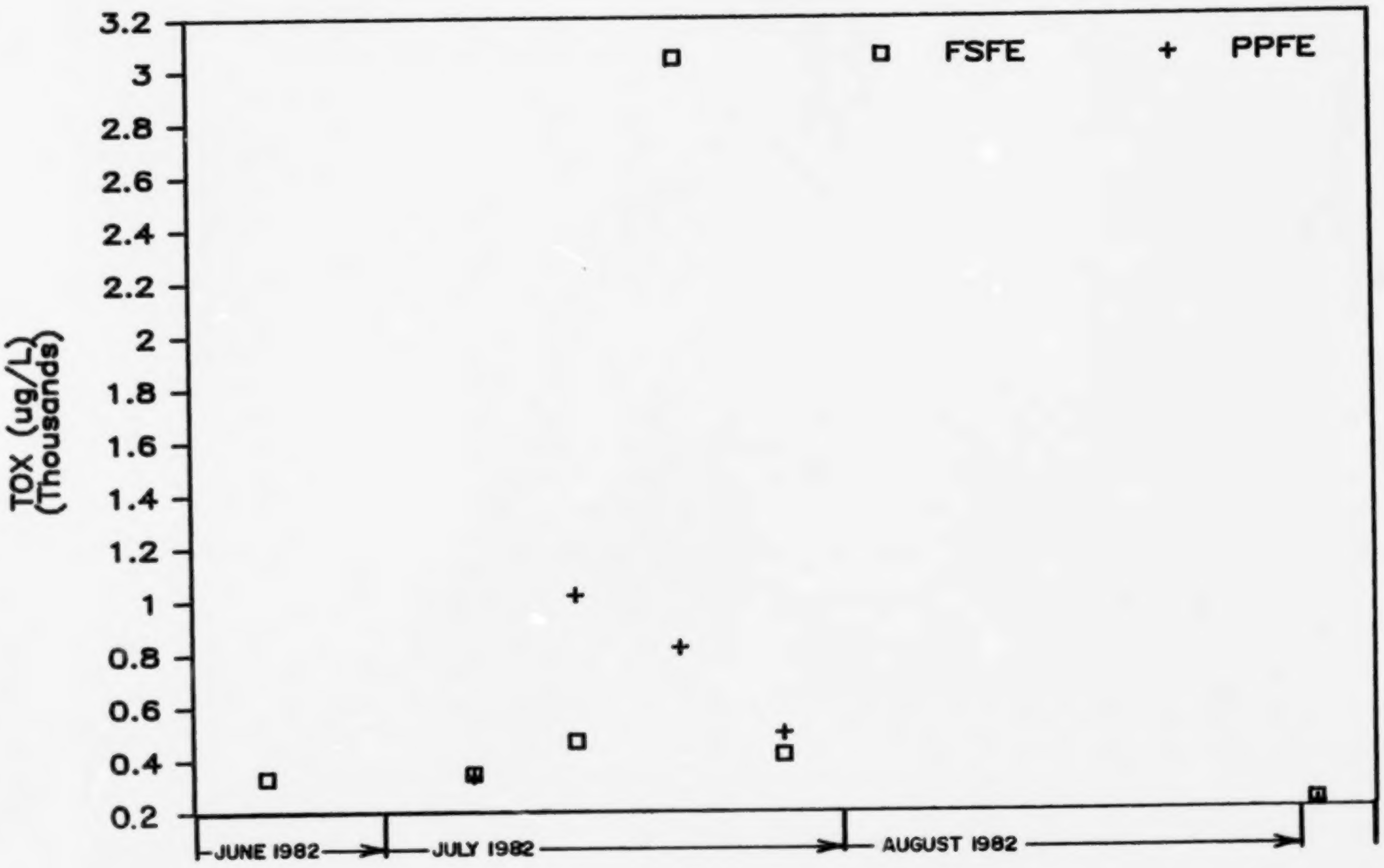


Figure 10. Performance comparison of pilot plant versus full-scale operation in regard to TOX.

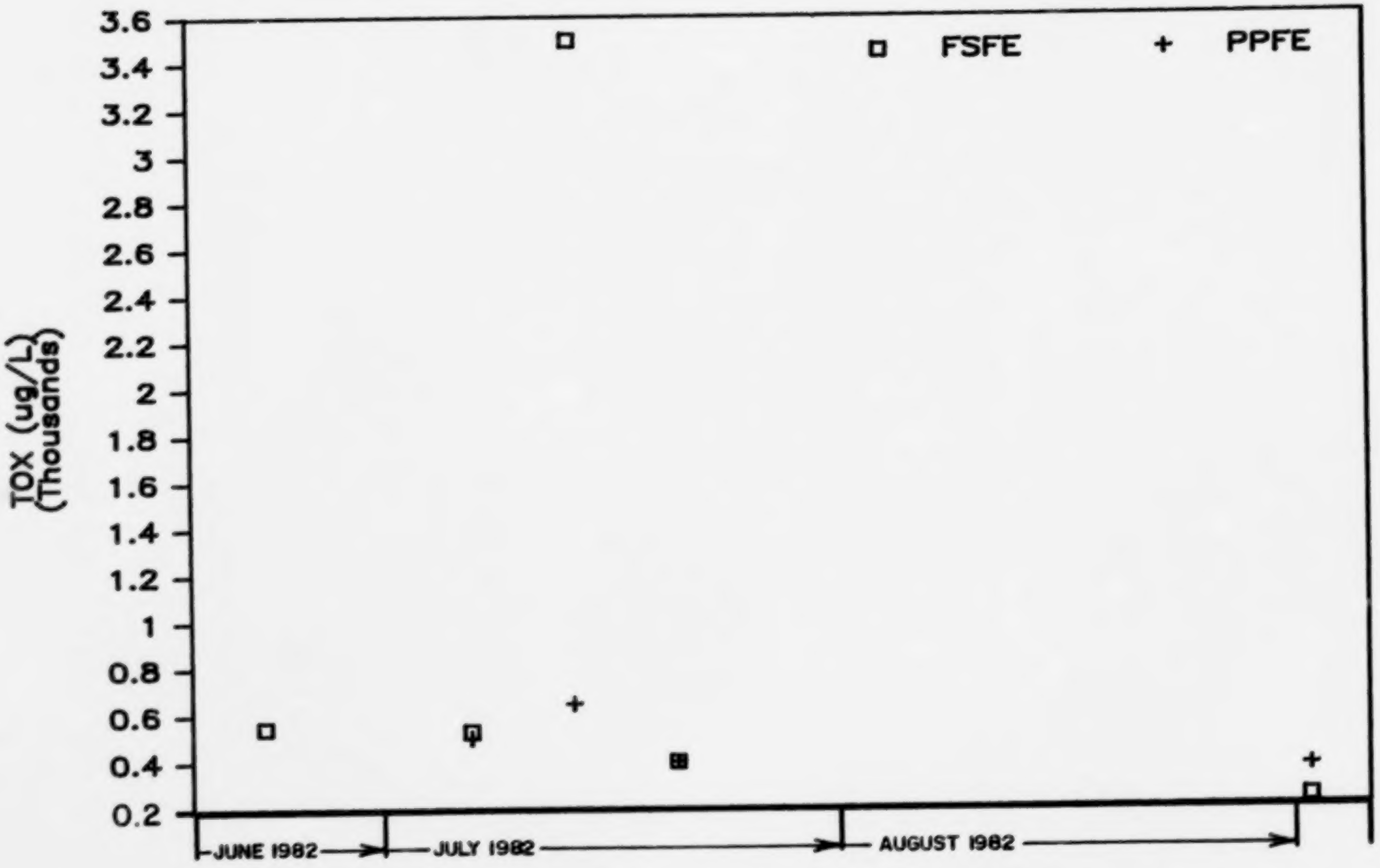


Figure 11. Performance comparison of pilot plant versus full-scale operation in regard to terminal TOX.

Conventional Treatment

The average TOC concentration of the raw water entering the pilot plant during the study was 5.2 mg/L. TOC removal across the clarifier was approximately 11 percent and approximately 8 percent across the filter.

Breakpoint chlorination, used in Mode 1, provided an opportunity to evaluate conventional treatment at Thornton, Colorado, for its effect on TTHM and TOX concentrations. A comparison of the TTHMFP and TOXFP for the raw water and the pilot plant filter effluent demonstrated the organic precursor removal capabilities of this conventional treatment process.

During Mode 1, TTHM in the full scale raw blend ranged from 0 to 40 ug/L, with an average concentration of approximately 11 ug/L. The TTHMFP of the full scale raw blend ranged from 87 to 1130 ug/L, with an average concentration of approximately 319 ug/L. The actual TTHM concentration of the pilot plant filter effluent ranged from 34 to 305 ug/L, with an average concentration of 91 ug/L. TTHMFP for the pilot plant filter effluent ranged from 72 to 379 ug/L with an average concentration of 191 ug/L. Conventional treatment appears capable of removing approximately 40 percent of the TTHMFP. It also appears that the actual TTHM formed during conventional treatment using breakpoint chlorination was approximately 30 percent of the TTHMFP of the raw water.

A bench scale study was conducted to compare coagulation performance for precursor removal at pH 5.0 and 7.8 because the literature indicators improved precursor removal when coagulation is operated at a slightly acidic pH. In this bench scale study, there was no significant difference noted in the removal of TTHMFP and TOXFP at the different pH values. Therefore, no modification was made to adjust the pH to a more acidic range in the pilot plant.

TOX in the full-scale raw blend ranged from 10 to 485 ug/L, with an average concentration of approximately 113 ug/L. TOXFP of the full scale raw blend ranged from 222 to 754 ug/L, with an average concentration of 430 ug/L. The pilot plant filter effluent TOX concentration ranged from 103 to 1020 ug/L, with an average concentration of 323 ug/L while the TOXFP concentration ranged from 160 to 649 ug/L with an average concentration of 374 ug/L. The TOXFP data show that approximately 15 percent of the organic precursors were removed during conventional treatment. Also, 75 percent of the TOXFP in the raw water was converted to TOX during the conventional treatment using breakpoint chlorination.

The ability of the flocculation and sedimentation processes to control the formation of chlorinated organics by organic precursor removal can be evaluated by comparing Mode 1 and Mode 2 data, since the breakpoint chlorination point was relocated downstream of the clarifier during Mode 2. Based upon average, instantaneous values, the conventional treatment processes were capable of removing 55 percent of the TTHM precursors and 30 percent of the TOX precursors.

Powdered Activated Carbon

During Mode 2 of the pilot plant operation, powdered activated carbon was added at dosages between 5 and 10 mg/L to the premix basin, with breakpoint chlorination occurring after clarification prior to the filter. In Mode 3 of the pilot plant operation, the process train remained identical to Mode 2 operation except no powdered activated carbon was added to the premix basin. Therefore, the data from these two modes of operation were used to assess the effectiveness of powdered activated carbon for removal of organic precursors. Because these modes were operated for a short period of time, limited TOC, TTHM, and TOX data were available.

Raw water quality was nearly equal in respect to organic content, with average TOC concentrations of 5.7 and 5.5 mg/L for Modes 2 and 3, respectively. The filter effluent TOC concentration averaged 4.5 mg/L for Mode 2 and 4.7 mg/L for Mode 3. Therefore, the data indicate that powdered activated carbon at those dosages is only slightly effective for TOC removal in the filter effluent. The instantaneous TTHM concentration in the filter effluent appears to be approximately the same irrespective of whether powdered activated carbon is used. The average TTHM concentrations were 33.7 ug/L for Mode 2 and 35.8 ug/L for Mode 3.

As with the TTHM data, the TOX concentration is not significantly different with and without powdered activated carbon addition. The data showed a slightly higher average TOX concentration for Mode 2 of 189 ug/L compared with the concentration for Mode 3 of 142 ug/L.

Granular Activated Carbon Performance

The performance of the GAC columns was analyzed using data from Modes 1 and 4. The methods of disinfection used were breakpoint chlorination in Mode 1 and breakpoint chlorination followed by ammoniation in Mode 4. The period of time over which the GAC columns were operated during these modes was of adequate length to determine the breakthrough characteristics of the columns. Samples that were analyzed to determine GAC performance were the effluent from column 10-6, simulating a post filtration GAC process, the effluent from column 11-6, simulating a retrofit of the existing filters, and the effluent from column 12-6, which simulates replacing the filters with a GAC process. The carbon columns were filled with virgin carbon at the beginning of each mode. Columns were backwashed on a routine basis during operation.

The average TOC concentration of the granular activated carbon influent was 4.6 mg/L for the columns receiving clarifier effluent and 4.3 mg/L for the columns receiving filter effluent. The average TTHM concentrations during Mode 1 were 85 ug/L for clarifier effluent and 91 ug/L for filter effluent. The respective concentrations during Mode 4 were 23 and 26 ug/L. Therefore, the two sets of carbon columns received water with approximately the same quality with respect to TOC and TTHM. The relative TOX concentrations were similar.

Results from the pilot studies indicate that, after a column is placed into service with virgin GAC, the TOC concentration in the effluent was low and increased almost immediately until it reached a steady state concentration. In all cases, this steady state concentration was reached in approximately 50 to 60 days. The effluent concentrations from Columns 10-6 and 12-6 were approximately equal, while the effluent concentration from Column 11-6 was slightly higher. The contact time through Column 11-6 was only half the contact time through Columns 10-6 and 12-6. These data are plotted in Figures 12 and 13 for Modes 1 and 4, respectively.

The GAC columns performed differently in regard to TTHM as compared to TOC. During Modes 1 and 4, the TTHM concentration in the effluent from the GAC columns remained below 5 ug/L for approximately 30-70 days, depending on the column. After that period of time, the TTHM concentration in the effluent began to increase. It appears that the TTHM concentration reaches a longer term steady state during which a degree of removal can still be maintained. As with the TOC data, the TTHM removal of columns 10-6 and 12-6 is nearly equal. The TTHM concentration in the effluent from these two columns remained below 5 ug/L for approximately 70 and 100 days, for Modes 1 and 4, respectively. TTHM concentration in the effluent from column 11-6 remained below 5 ug/L for only 30 and 50 days for Modes 1 and 4, respectively. The steady state level for column 11-6 was higher than that level for columns 10-6 and 12-6, presumably a result of the difference in contact time. Figures 14 and 15 contain plots of the TTHM data versus time for Modes 1 and 4, respectively.

THMFP is an important parameter for judging the performance of the GAC process. Since the water is dechlorinated during the GAC process, the effluent must be chlorinated prior to delivery to the customer. TTHMFP data plotted in Figures 16 and 17 are for samples which have been dosed with chlorine at a level that is 2 mg/L higher

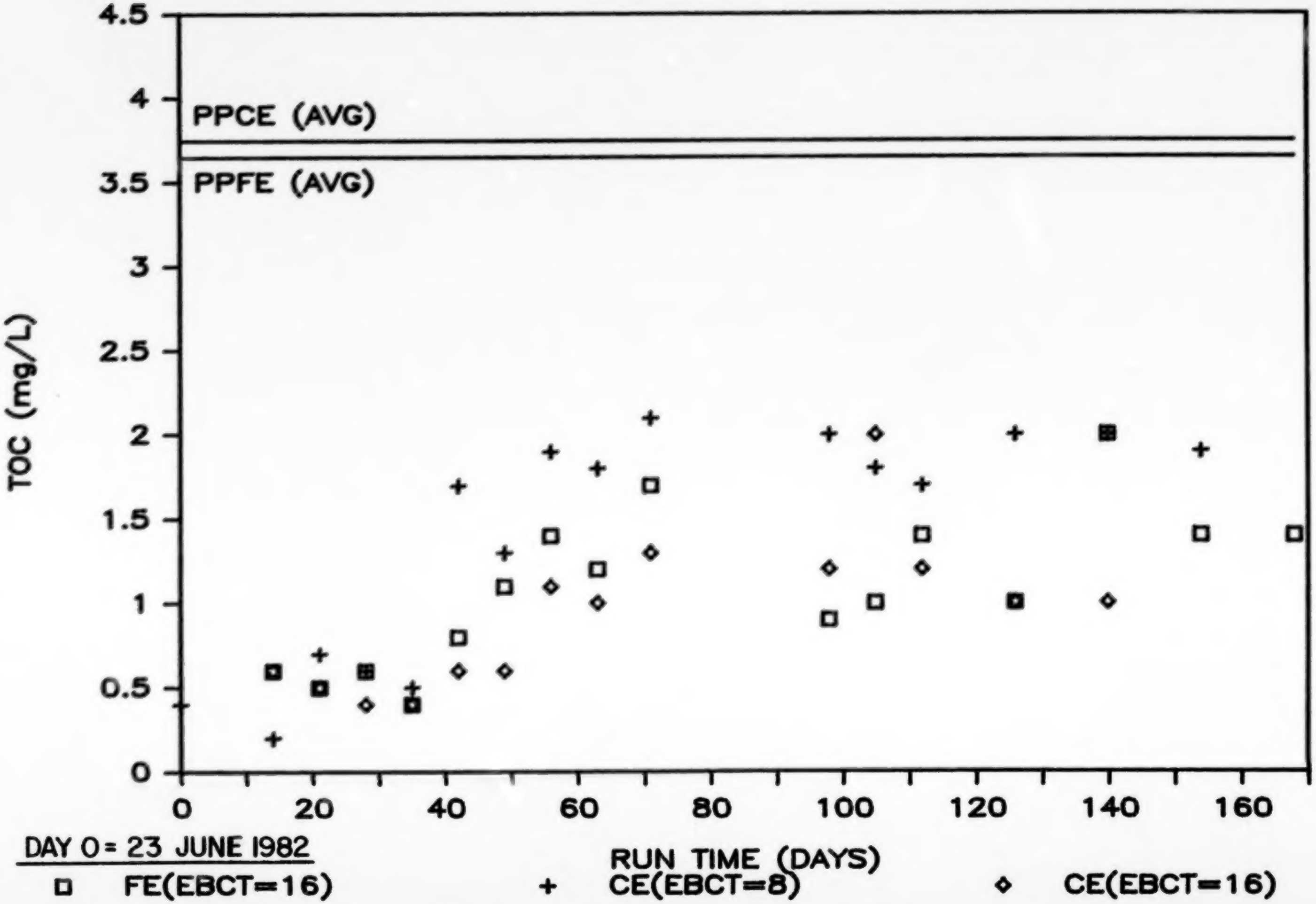


Figure 12. GAC performance evaluation using TOC removal data for Mode 1 - Free Chlorination.

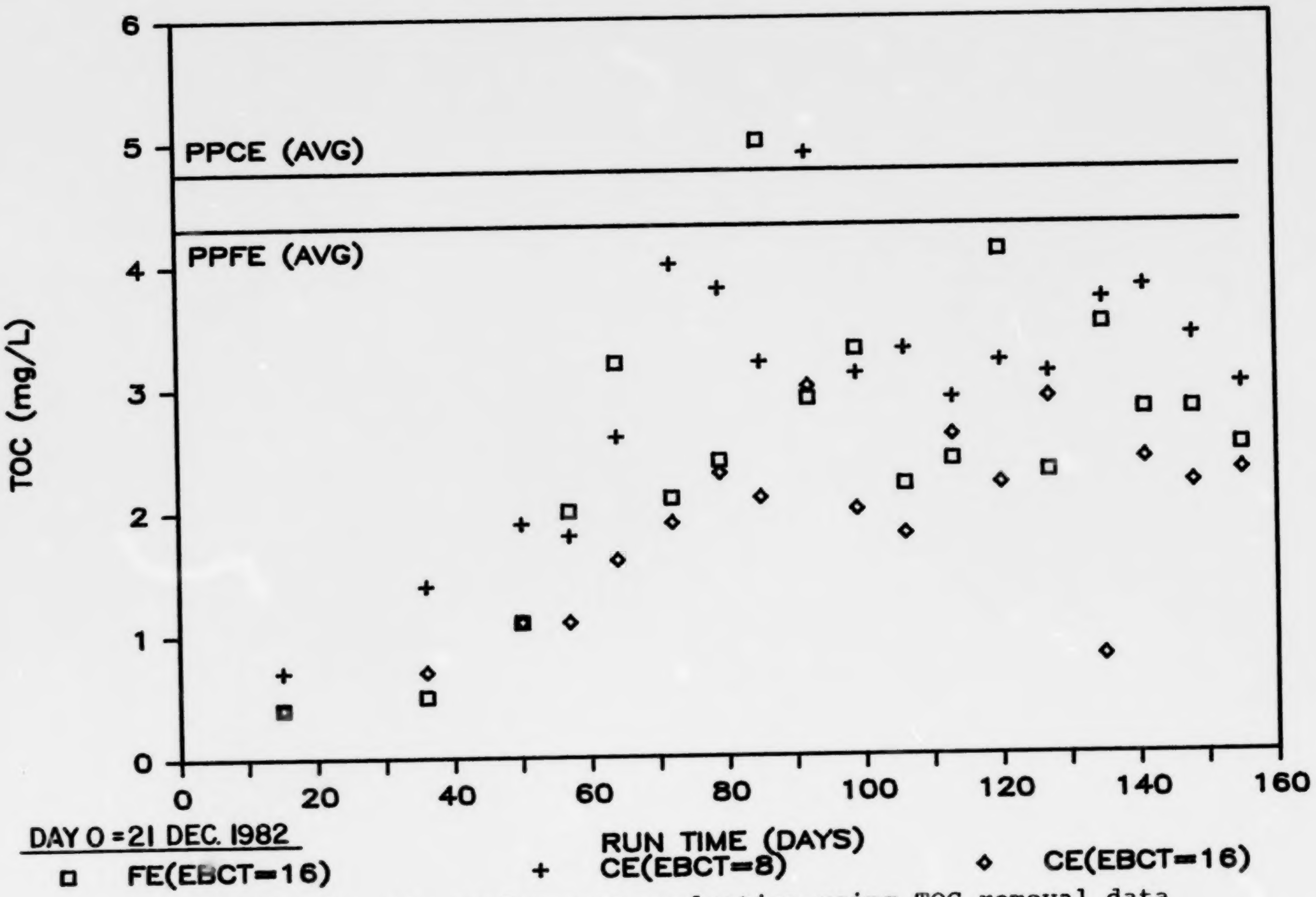


Figure 13. GAC performance evaluation using TOC removal data for Mode 4 - Postammoniation.

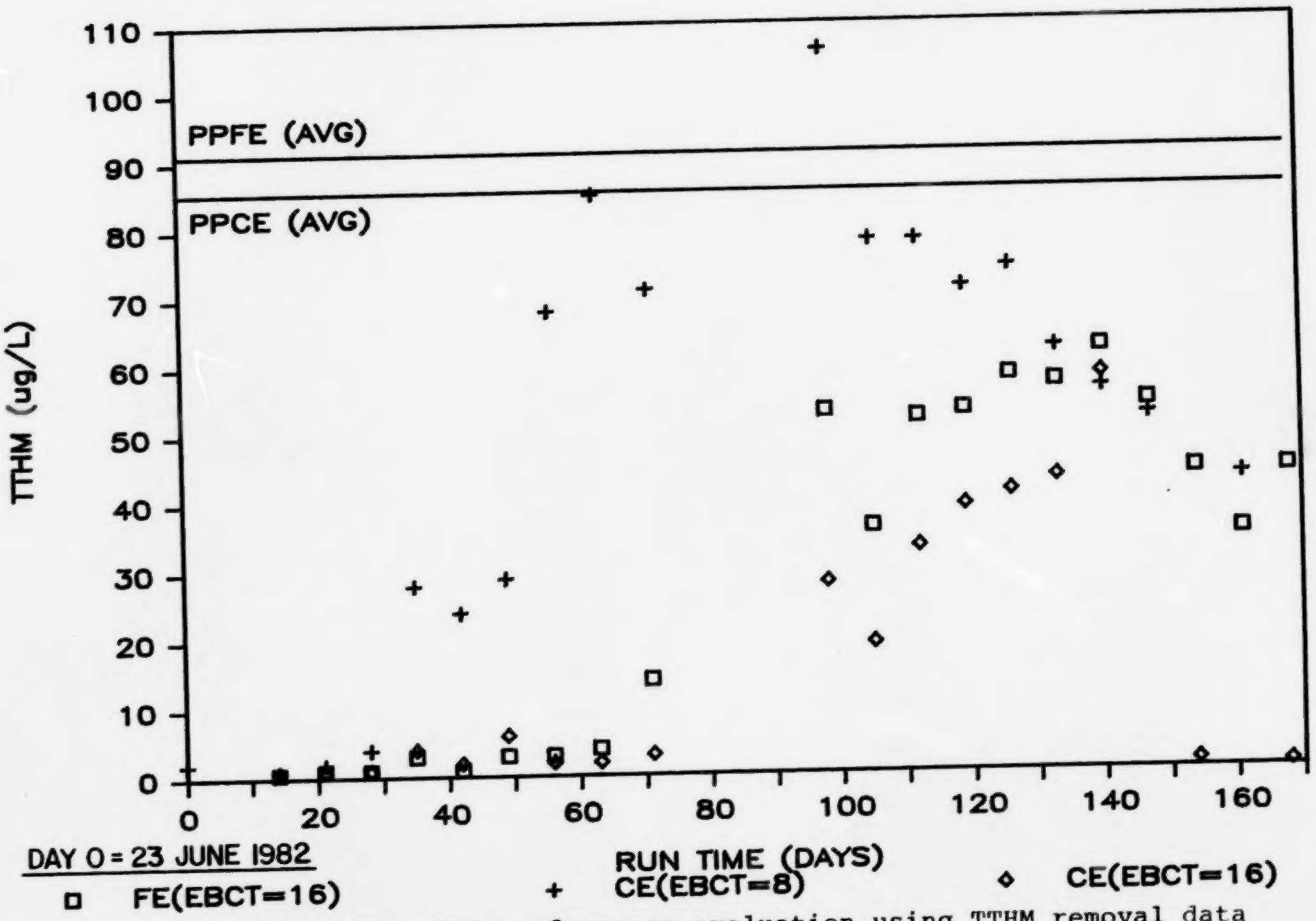


Figure 14. GAC performance evaluation using TTHM removal data for Mode 1 - Free Chlorination.

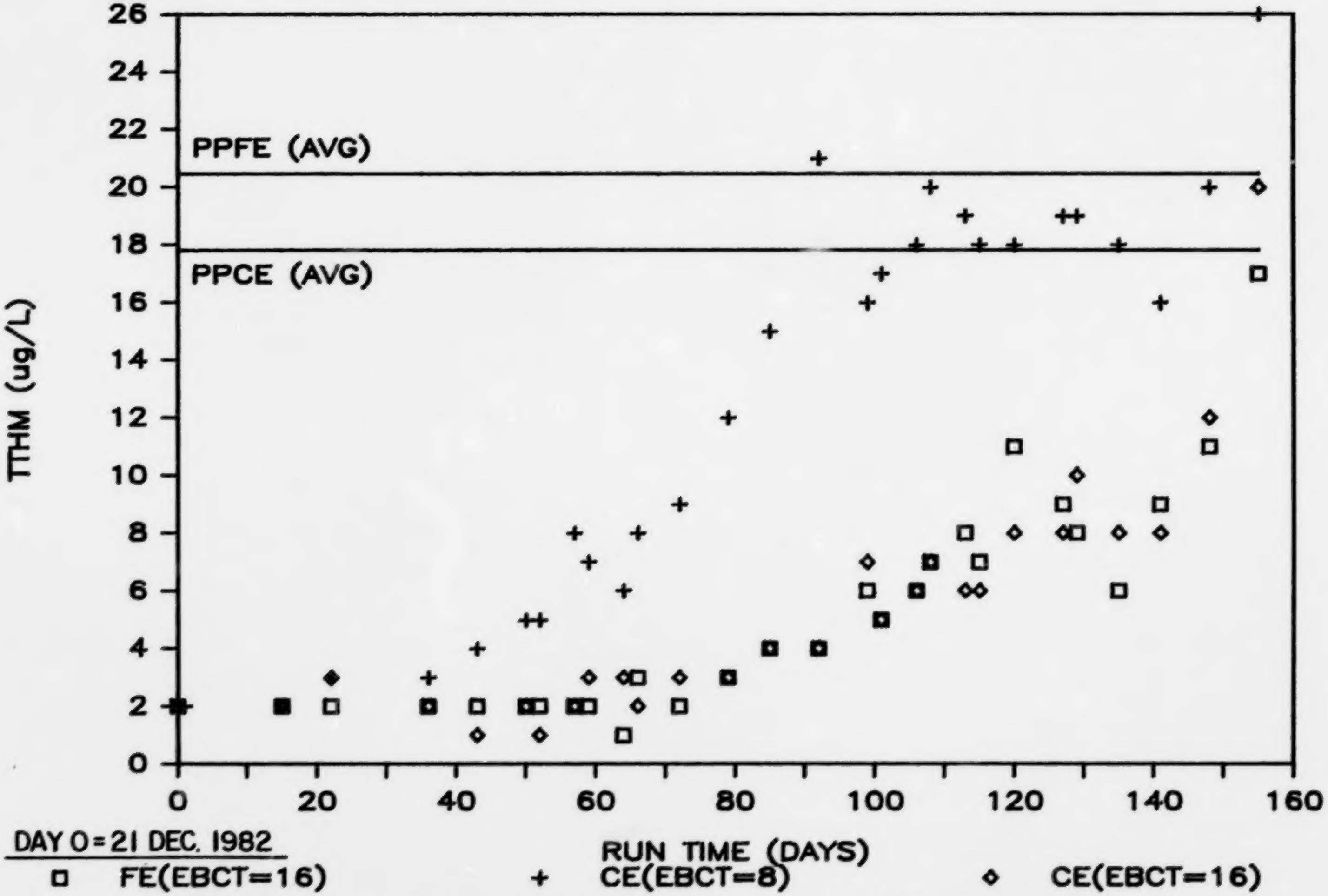


Figure 15. GAC performance evaluation using TTHM removal data for Mode 4 - Postammoniation.

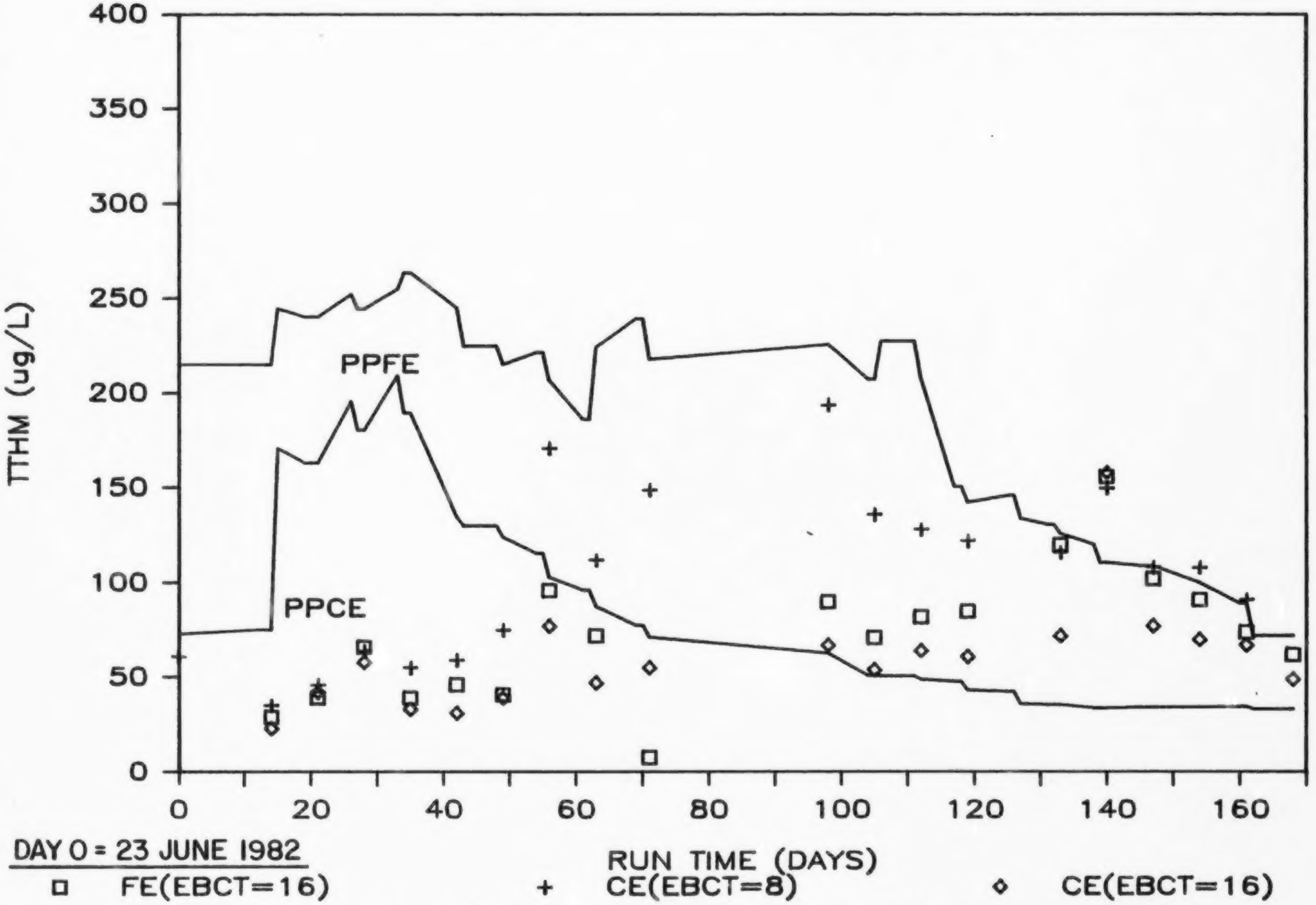


Figure 16. GAC performance evaluation using TTHMFP removal data for Mode 1 - Free Chlorination.

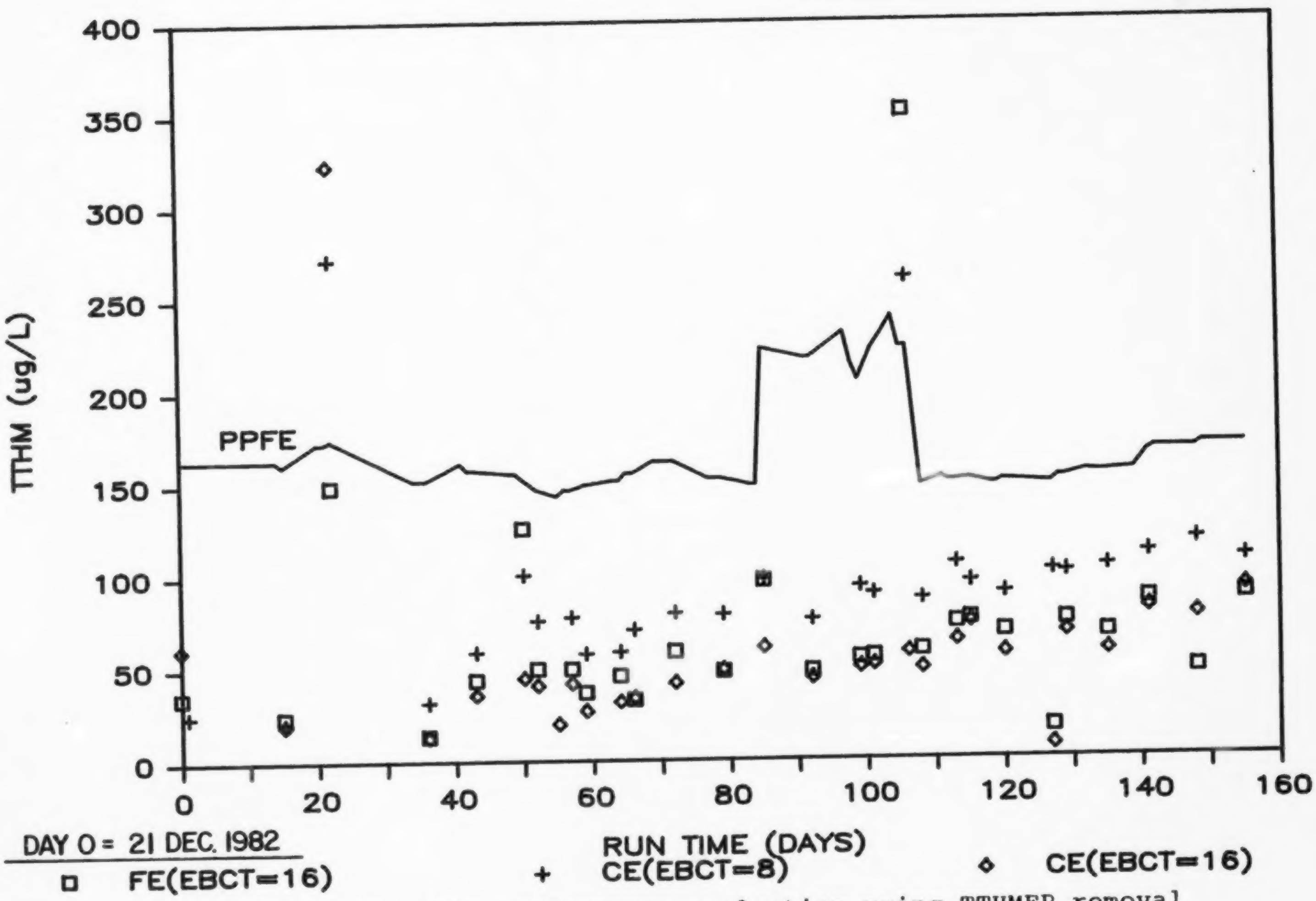


Figure 17. GAC performance evaluation using TTHMFP removal data for Mode 4 - Postammoniation.

than the one hour chlorine demand. The TTHMFP concentration in the effluent from the GAC columns began below 50 ug/L and then increased to a quasi-steady state concentration after 30 to 50 days for Mode 1 and 40 to 90 days for Mode 4. The erratic spikes evident in the figures may be due to the chromatographic effect of the GAC and variations in the influent concentration. Because of the difference in contact time, TTHMFP in the effluent from column 11-6 began increasing sooner and reached a higher level than the effluents from columns 10-6 and 12-6. The GAC columns may have been effective in maintaining the effluent TTHMFP concentration below 100 ug/L for approximately 80 days, but because of the erratic nature of the data, this cannot be stated with much certainty.

The TOX data were fairly erratic. It was difficult to determine exactly how the GAC columns performed with respect to TOX. TOXFP data for Mode 4 operation demonstrated a similar trend to that found for the TTHMFP. A plot of these data is included in Figure 18. The TOXFP data for Mode 1 was limited and a trend could not be developed.

Alternative Disinfectants

During the pilot plant study, alternative disinfectants were examined for control of chlorinated organic byproducts. Initially, the primary disinfection process was breakpoint chlorination. Breakpoint chlorination was used in Mode 1 where chlorine was added to the premix basin, and in Modes 2 and 3 where chlorine was added after the clarifier. The disinfection process used during Mode 4 was chloramination using a post-ammoniation process. In this process, chlorine was added to the premix basin to obtain breakpoint chlorination, then ammonia was added to the effluent of the premix basin to form chloramines. Chloramination was also practiced during Mode 5, but a chloramine solution was formed off-line and injected into the premix basin. A dual disinfection process was used for Mode 6 in which a chlorine dioxide solution and a chloramine solution that was generated off-line were added to the premix basin.

The water quality of the pilot plant filter effluent was used to determine the performance of the alternative disinfectants. Formation of chlorinated organic byproducts was determined using TTHM and TOX analyses. Bacteriological quality of the filter effluent was determined using both total coliform and standard plate count techniques. From these, the bactericidal efficiency of the alternative disinfectants could be determined.

Chlorinated Organic Formation

THM data from Modes 1, 4, 5, and 6 are plotted in Figures 19 through 22, respectively. The data presented are the TTHMFP of the full-

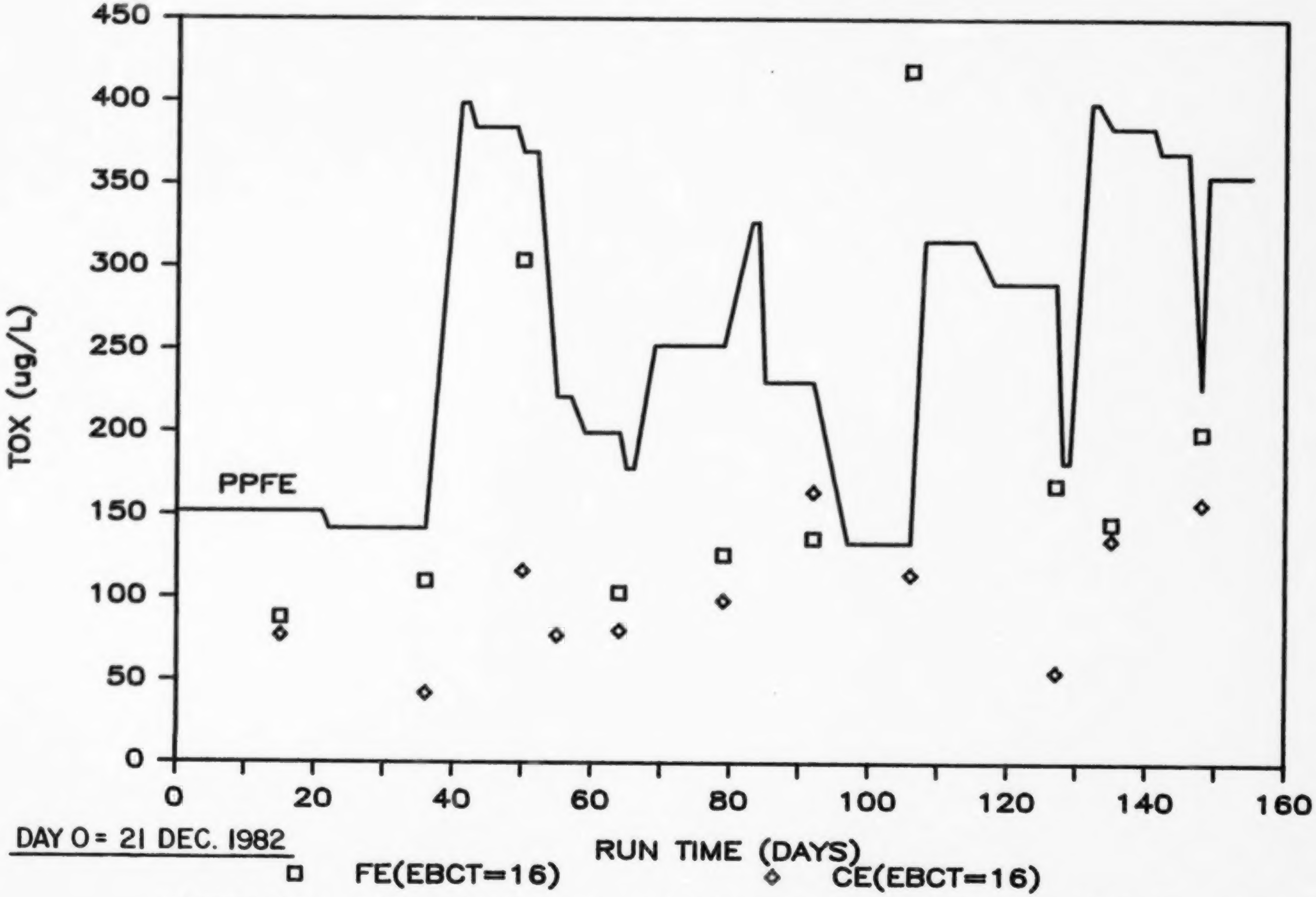


Figure 18. GAC performance evaluation using TOXFP removal data for Mode 4 - Postammoniation.

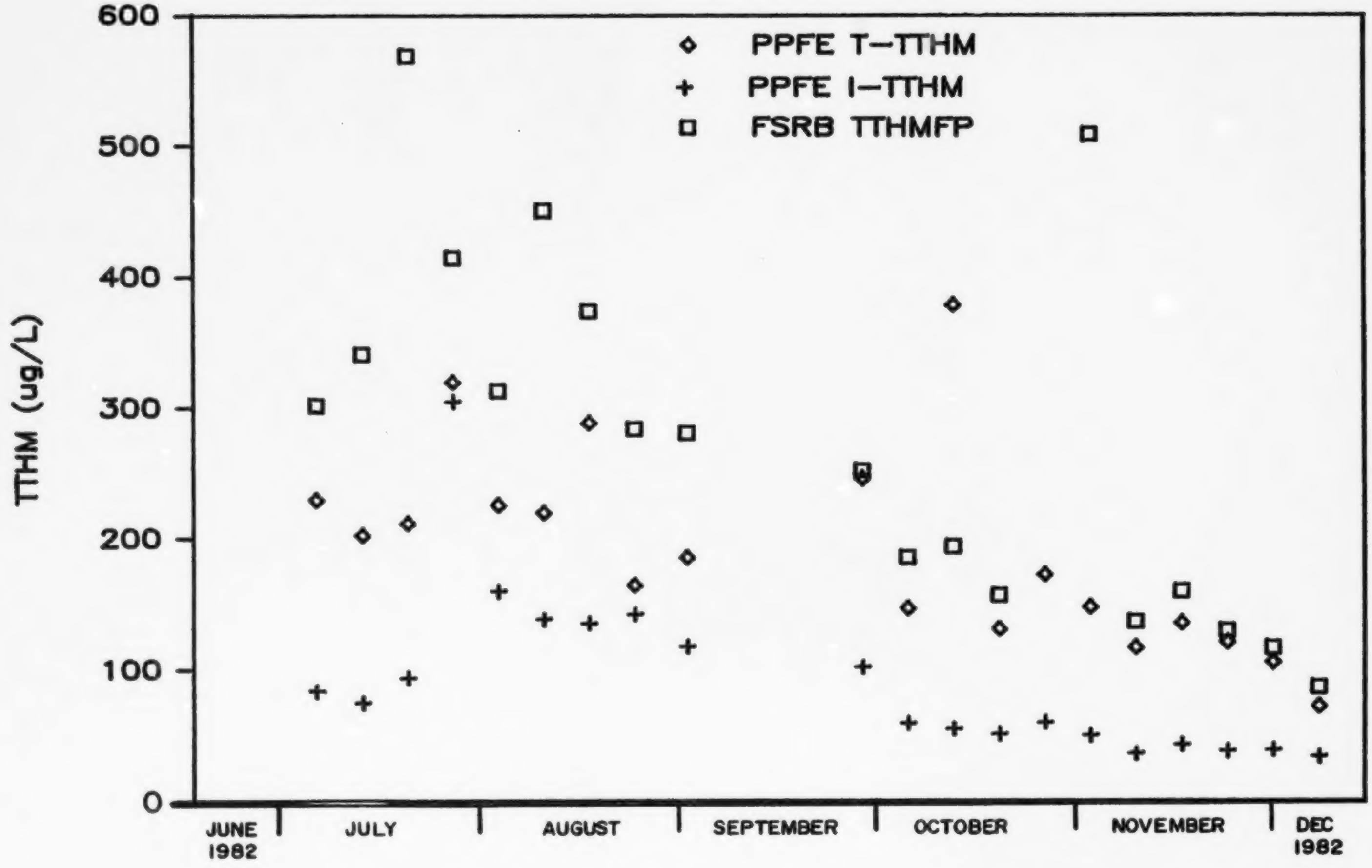


Figure 19. Alternative disinfectant evaluation using TTHM formation data for Mode 1 - Free chlorination.

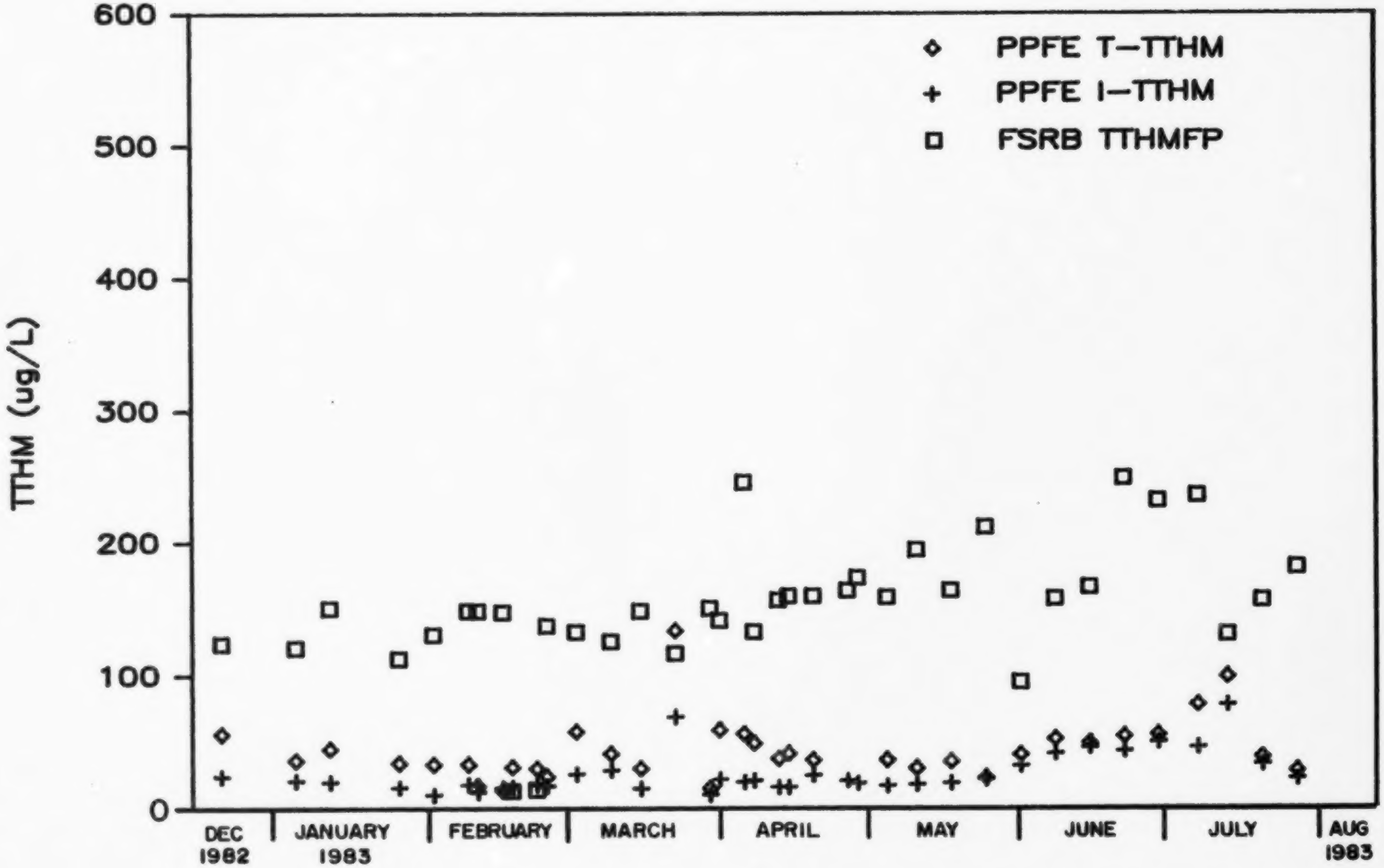


Figure 20. Alternative disinfectant evaluation using TTHM formation data for Mode 4 - Postammoniation.

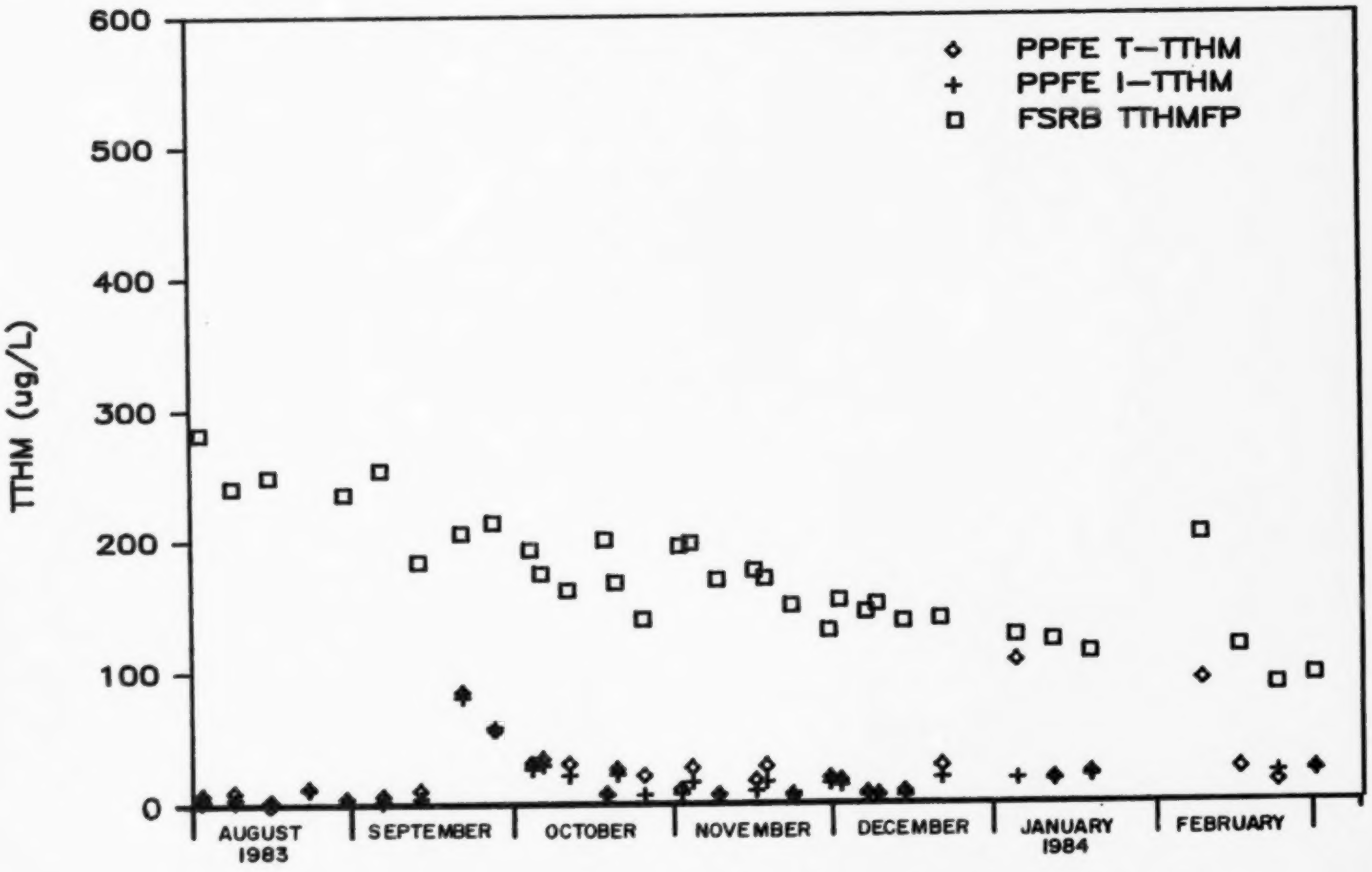


Figure 21. Alternative disinfectant evaluation using TTHM formation data for Mode 5 - Preformed chloramines.

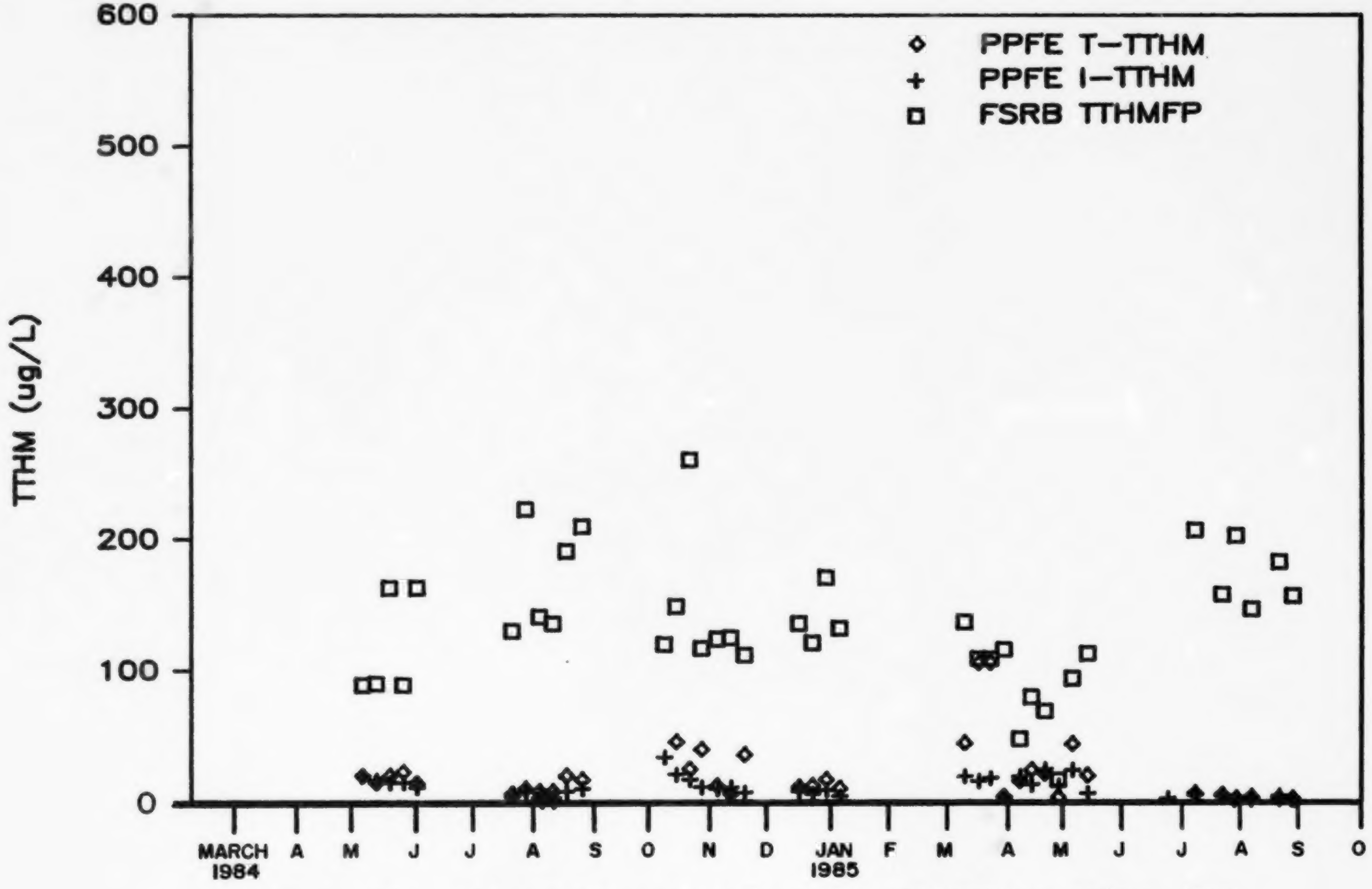


Figure 22. Alternative disinfectant evaluation using TTHM formation data for Mode 6 - Dual Disinfection.

scale raw blend, the instanteous TTHM of the pilot plant filter effluent, and the terminal TTHM of the pilot plant filter effluent. TTHMFP for the full-scale raw blend was determined by spiking the sample with chlorine at a dosage of 2 mg/L greater than the one hour demand. The sample was then stored for a five day period prior to analysis. TTHMFP for the raw blend is shown for the various modes to provide an indication of the raw water quality entering the pilot plant. Concentrations fluctuate on a seasonal basis but are fairly equal for the various modes. An exception to this is seen in Figure 21 for Mode 5. Mode 5 was operated from late summer to early spring, a period when a decrease in the TTHMFP of the full-scale raw blend was observed.

The terminal TTHM for the pilot plant filter effluent was determined by taking the filter effluent sample and storing it for a five-day period. A holding period of five days was selected for the terminal TTHM analysis because this is approximately the maximum detention time in the distribution system. It was also noted in special studies that TTHM increased during this holding period. These results will be presented in Section 8 - Batch Studies of Chlorination Characteristics.

The average instantaneous TTHM concentrations in the pilot plant filter effluent for Modes 1, 4, 5, and 6 are shown in Figure 23. The average instantaneous TTHM concentration for Mode 1 was approximately 80 ug/L, approximately 25 ug/L for Mode 4, approximately 15 ug/L for Mode 5, and approximately 10 ug/L for Mode 6. The average terminal TTHM concentrations were approximately 190 ug/L for Mode 1 and 40 ug/L for Mode 4. The higher concentration for Mode 1 results from the free chlorine available during storage, while Mode 4 has no free chlorine because of post-ammoniation. The data show that there is not a significant increase in the TTHM concentration between the instantaneous and terminal values for Modes 5 and 6. These terminal values indicate the expected maximum concentration of TTHM in the distribution system for each mode of operation.

TOX is a nonspecific parameter for indication of chlorinated organics. TOX data for Modes 1, 4, 5 and 6 are plotted in Figures 24 through 27 in a fashion similar to those provided for the TTHM data. In addition, a bar chart showing the relative levels of the average instaneous TOX in the pilot plant filter effluent for these modes is included in Figure 28. The general trends for the TOX data is similar to that observed for the TTHM data.

Bactericidal Efficiency

Total coliform data for the pilot plant filter effluent show reduction to less than the detection limit in nearly all cases for each alternative disinfectant. Therefore, because of its greater sensitivity, SPC was used as a means for examining the bactericidal

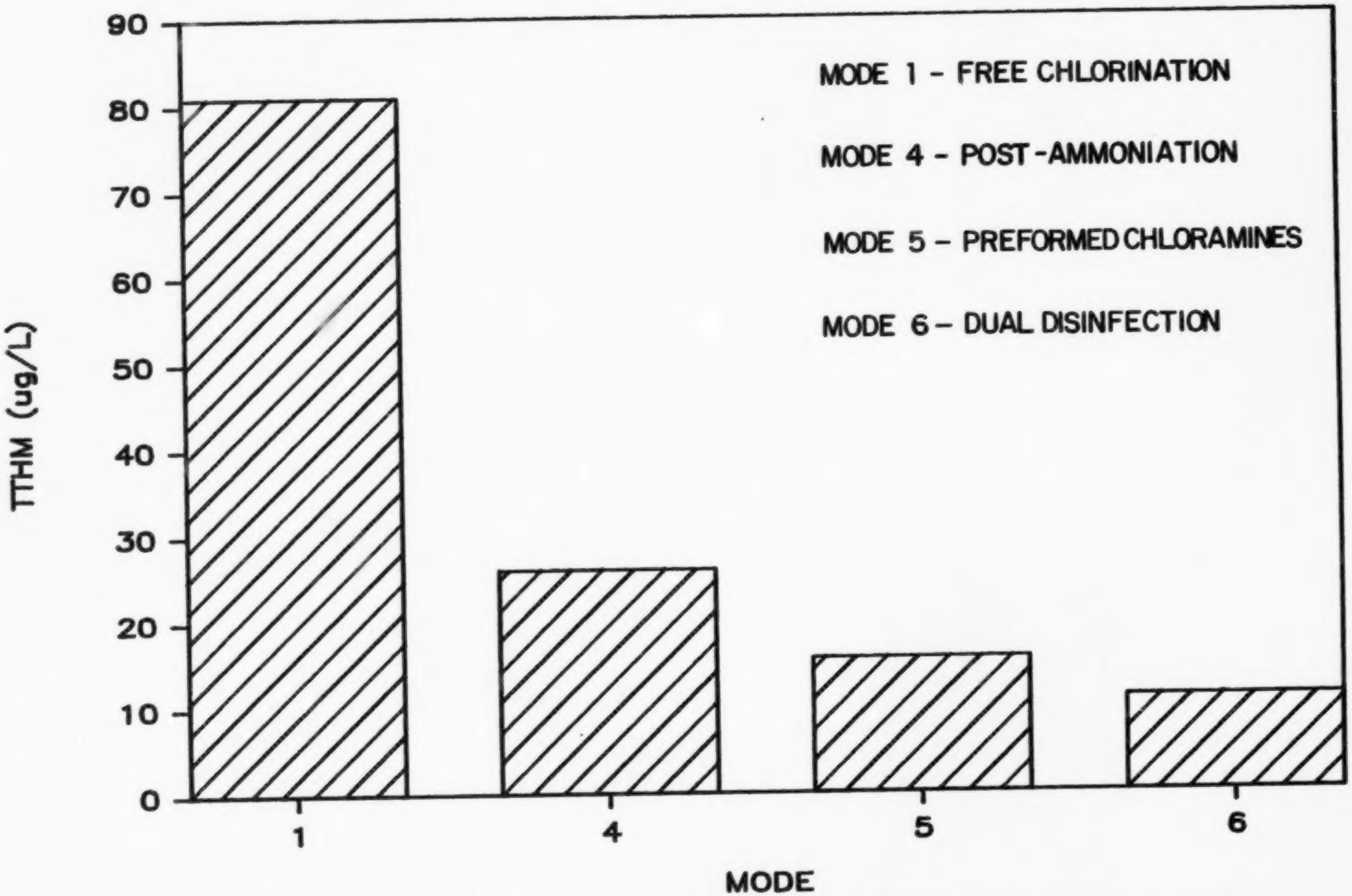


Figure 23. Alternative disinfectant evaluation using average instantaneous TTHM data.

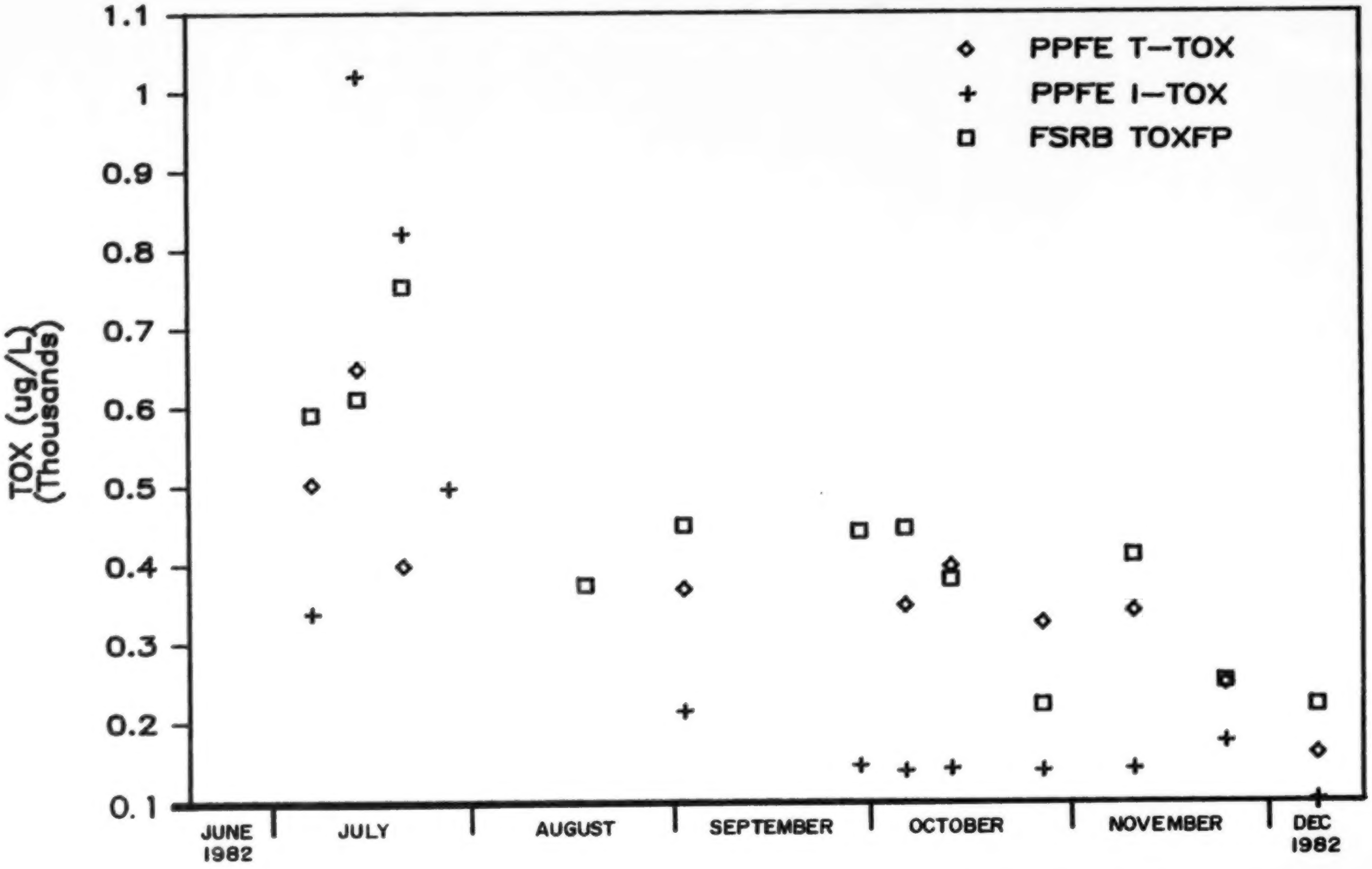


Figure 24. Alternative disinfectant evaluation using TOX formation data for Mode 1 - Free chlorination.

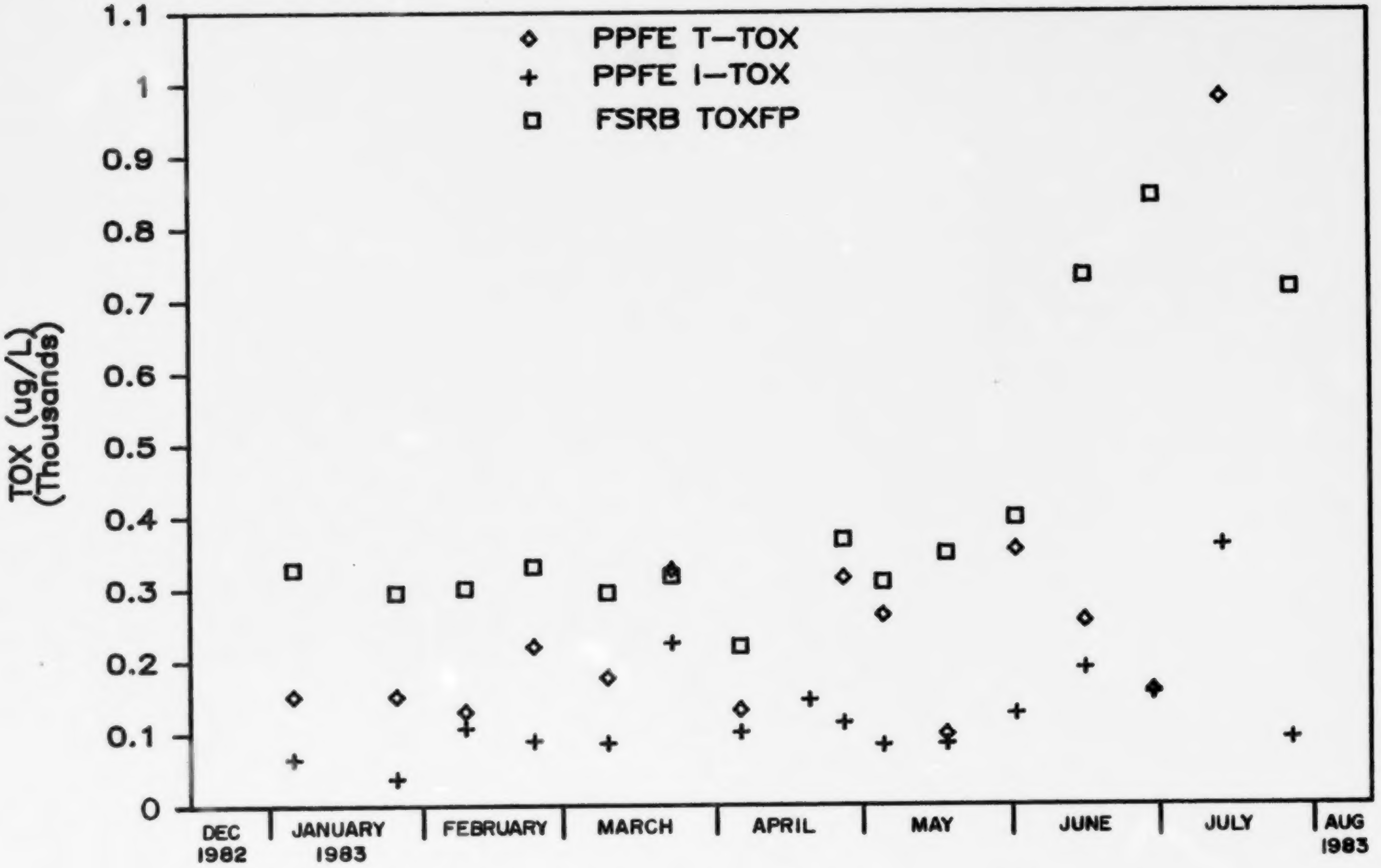


Figure 25. Alternative disinfectant evaluation using TOX formation data for Mode 4 - Postammoniation.

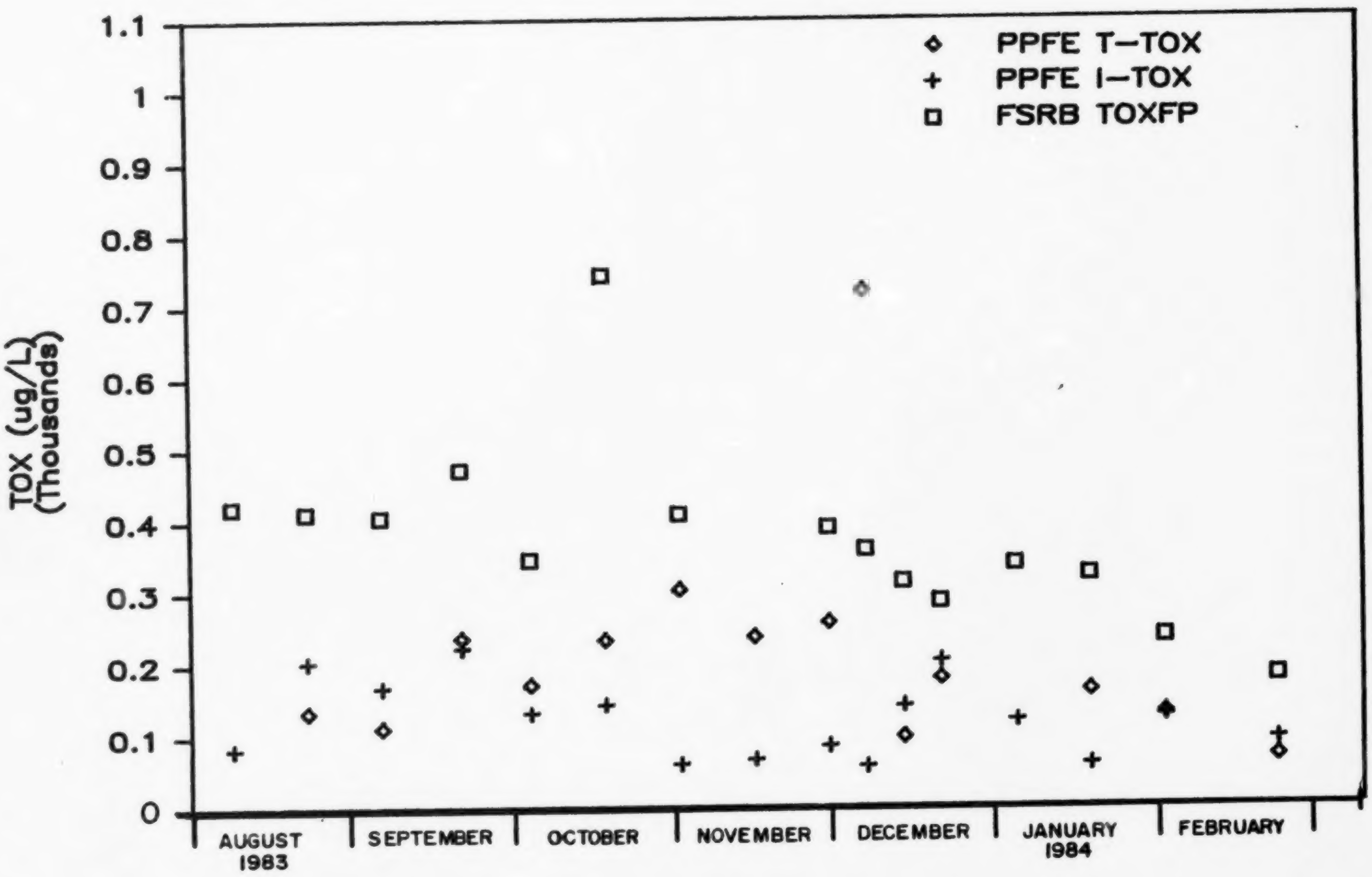


Figure 26. Alternative disinfectant evaluation using TOX formation data for Mode 5 - Preformed chloramines.

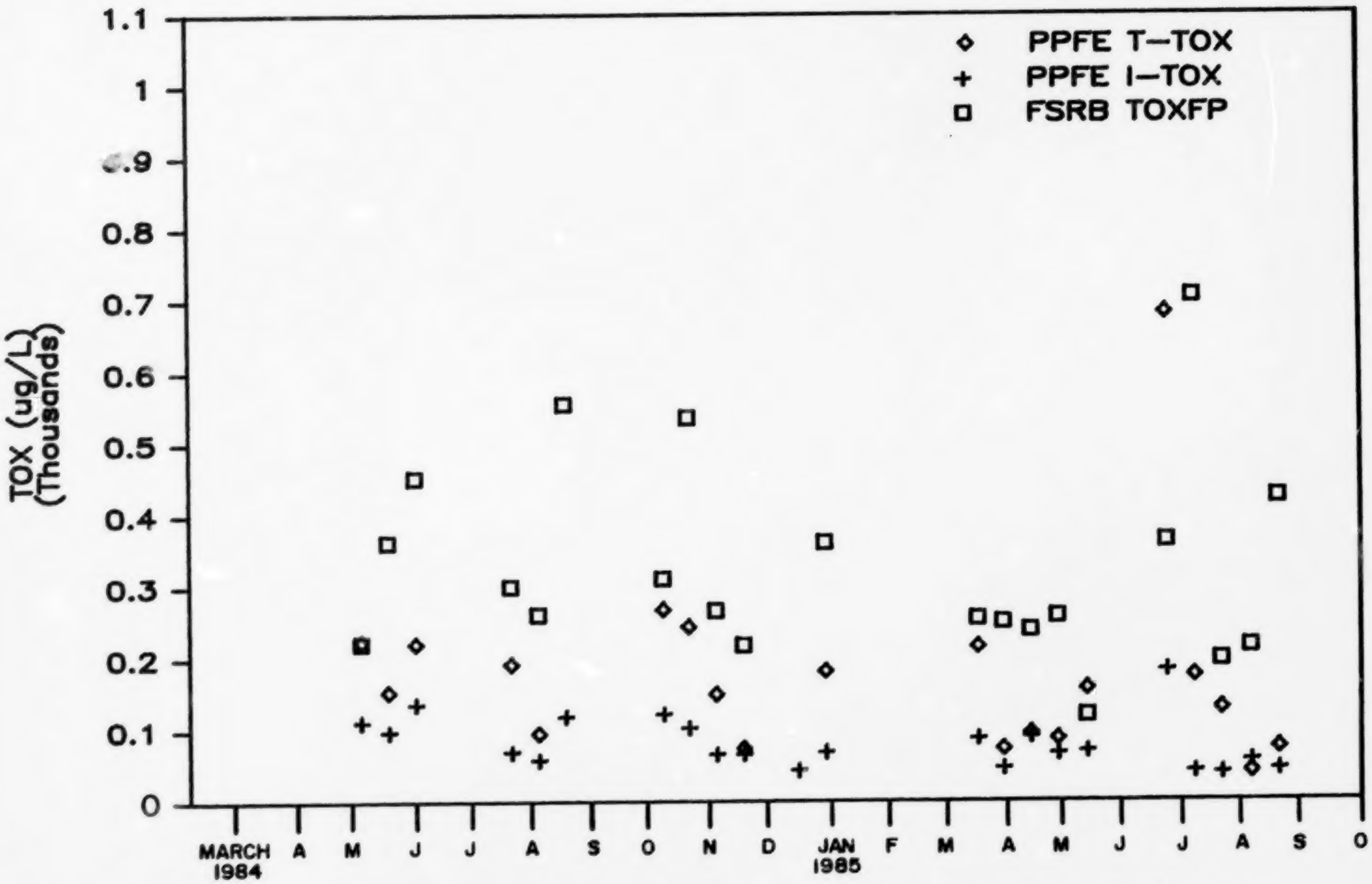


Figure 27. Alternative disinfectant evaluation using TOX formation data for Mode 6 - Dual Disinfection.

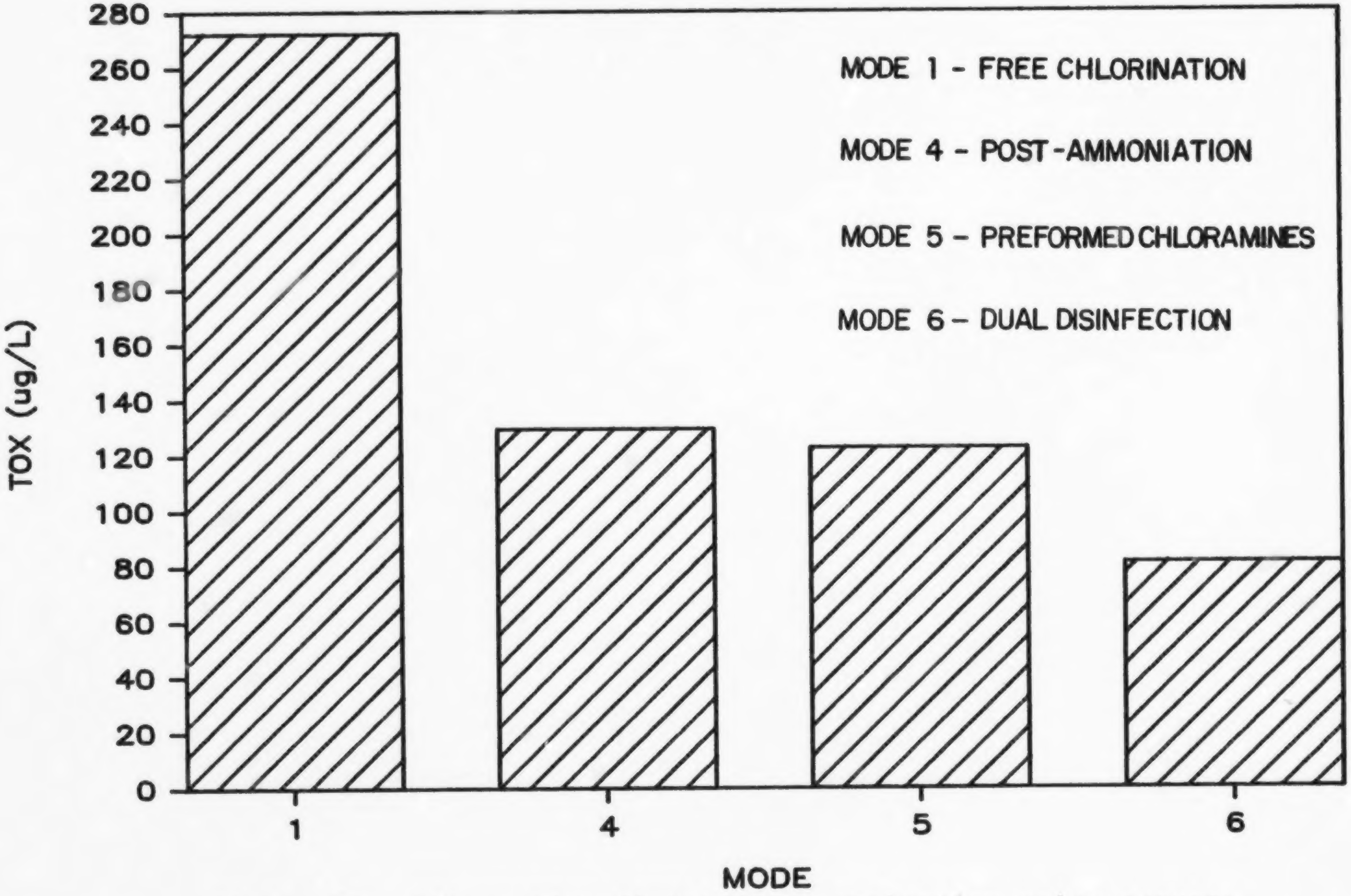


Figure 28. Alternative disinfectant evaluation using average instantaneous TOX data.

efficiency of the alternative disinfectants.

Probability distributions of the SPC data for the pilot plant filter effluent from Modes 1, 4, 5, and 6 are shown in Figure 29. Because of the distribution of the SPC data, bactericidal effectiveness of the alternate disinfectants cannot be evaluated using mean or median values. Probability distributions show that with breakpoint chlorination, or free chlorination, as practiced during Mode 1, a SPC of 10 per mL was achieved approximately 98 percent of the time. When practicing chloramination using the post-ammoniation method as in Mode 4, a SPC of 10 per mL was achieved only 87 percent of the time. When using a chloramine solution generated off-line for chloramination as was practiced during Mode 5, a SPC of 10 per mL was achieved only 76 percent of the time. When chlorine dioxide is used as the primary disinfectant in a dual disinfection system as practiced during Mode 6, a SPC of 10 per mL was again achieved approximately 97 percent of the time. The relative bactericidal efficiency of the alternate disinfectants is consistent with that found in the literature.

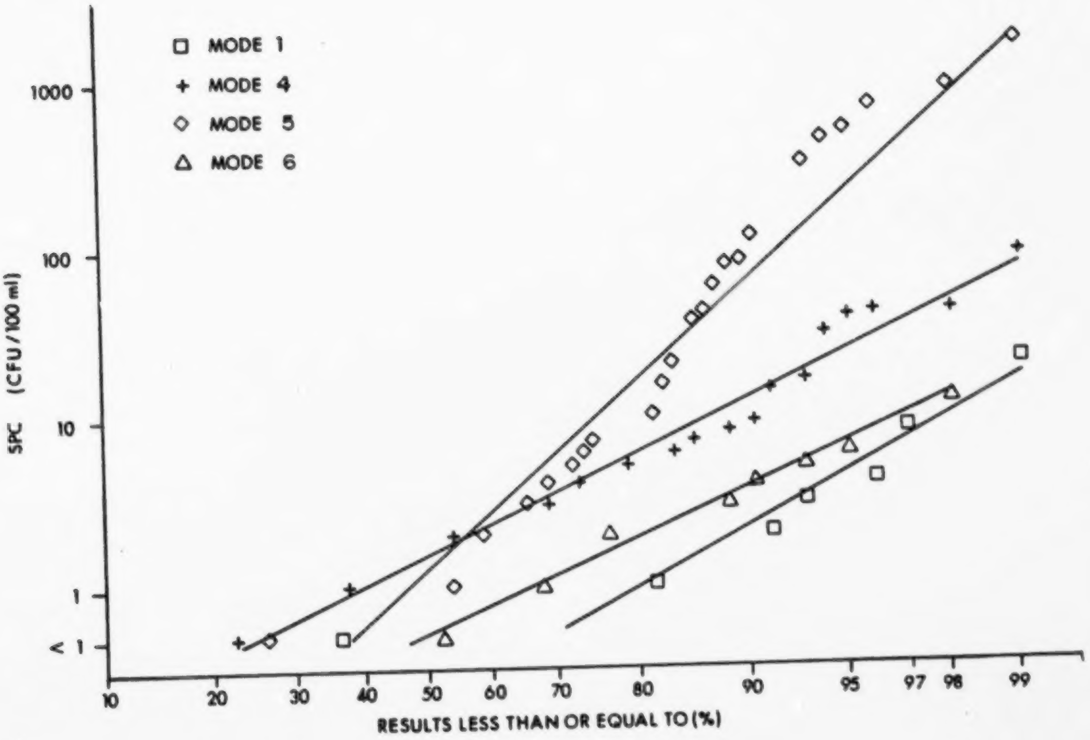


Figure 29. Alternative disinfectant evaluation using standard plate count data.

SECTION 7

RAW WATER MONITORING

PROGRAM

The purpose of the raw water monitoring program was to characterize the water sources available to Thornton according to quality so that potential variations in raw water quality can be considered in comparing respective phases of pilot plant operation. Additionally, based upon these characterizations, the City of Thornton can compare the raw water sources to one another, recognize the annual changes in water quality for each source, and then plan their raw water supplies using water quality as a basis. An initial benefit of the raw water monitoring program was the reduction in the raw water ammonia concentration to the Columbine Water Treatment Plant. Because of results of initial analytical work, the primary raw water source was changed and lower raw water ammonia concentrations were the result.

The raw water monitoring program will continue as an ongoing water quality tool for the City of Thornton. It is hoped the program will lead to sound decisions, not only for the use of current water sources, but for the acquisition of future sources.

Sampling

The sample points selected for the Raw Water Monitoring Program are listed in Table 6 and shown on the map in Figure 30. Currently, the primary raw water sources to the Columbine Plant are a series of gravel lakes and a shallow well field. The gravel lakes and well field are located along the South Platte River. Depending on river flow and groundwater level, the water for these two sources can be alluvial water from the river or groundwater flowing towards the river. In the past, water from Clear Creek has also been diverted to the plant through the Lower Clear Creek Ditch. Water from Standley Lake, a reservoir supplied with water from Clear Creek, can also be directed to the Columbine Plant through a pipeline.

The South Platte River upstream of the Denver Metropolitan Wastewater Disposal District No. 1 (Metro) discharge best

TABLE 6. RAW WATER MONITORING PROGRAM SAMPLE POINTS

Designation	Description
Gravel Lakes	Sampled from Northeast Tani Lake at a point five to six feet from shore.
Well Field	Sampled from the operating well with the highest NH_3-N concentration at the time of sampling.
Burlington Ditch	Sampled at the Burlington Ditch diversion point prior to entering the Gravel Lakes. The Burlington Ditch at this location is influenced by the Denver Metro Sewage discharge, since effluent from the wastewater facility is pumped into the ditch.
South Platte River Upstream	Located approximately 0.5 miles upstream of Denver Metro Sewer discharge. Sampled at 58th Avenue Bridge and South Platte River, five to six feet from shore, in an area of high flow.
South Platte River Downstream	Approximately 2 miles downstream of the Denver Metro Sewer discharge. Sampled at Union Pacific Railroad Bridge (approximatly 80th Avenue) and South Platte River, five to six feet from shore, in an area of high flow.
Lower Clear Creek	Located approximately 50 yards upstream of Columbine WTP intake headgate. Sampled at 86th Avenue and Lower Clear Creek Ditch, middle of ditch.
Standley Lake	Sampled at the City of Westminster's Semper WTP, prior to the screens. This water is piped from the bottom outlet of the lake, 100 feet from the face of the dam, 40 feet down.
Chatfield Reservoir	Sampled at Plum Creek and Highway 470, five to six feet from shore, in an area of high flow.

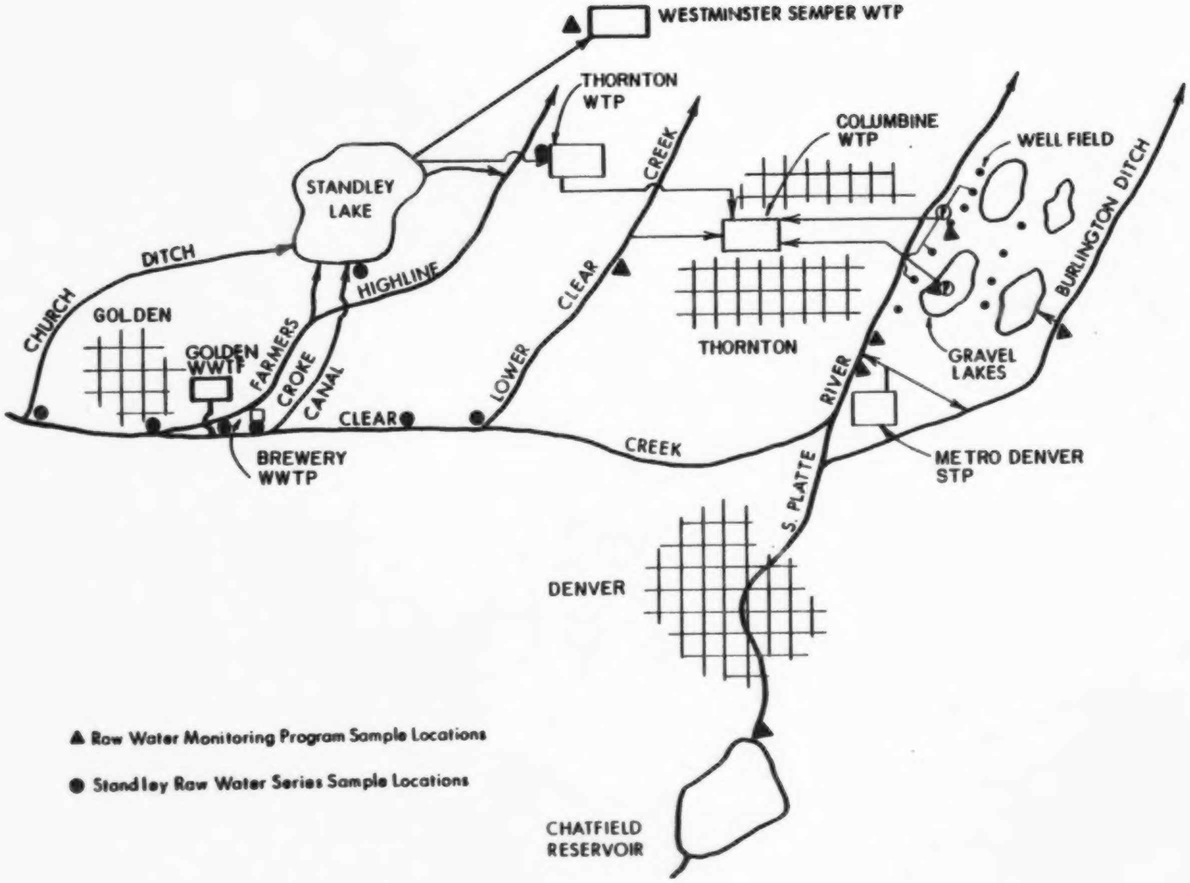

WESTMINSTER SEMPER WTP
THORNTON WTP
COLUMBINE WTP
WELL FIELD
BURLINGTON DITCH
STANDLEY LAKE
DITCH
CHURCH
GOLDEN
HIGHLINE
CREEK
CLEAR
LOWER
THORNTON
GRAVEL LAKES
GOLDEN WWTF
FARMERS
CROKE
CANAL
CLEAR
CREEK
RIVER
S. PLATTE
BREWERY WWTP
METRO DENVER STP
DENVER
▲ Raw Water Monitoring Program Sample Locations
● Standley Raw Water Series Sample Locations
CHATFIELD RESERVOIR

Figure 30. Raw water sample points.

represents the water that will be diverted through a new diversion canal and pipeline into the Gravel Lakes. Since Metro effluent can be pumped into the ditch, at a location tributary to the previous diversion, Thornton has changed their diversion procedures to minimize the effect of Metro on the Gravel Lakes. Depending on groundwater levels, the South Platte River downstream of the Metro discharge can have an effect on the quality of both the gravel lakes and well fields as previously mentioned. The Chatfield Reservoir sample provides an opportunity to monitor the background water quality trends of the South Platte River prior to entering the urbanized Denver Metropolitan area.

As a part of another water quality program, additional sampling was conducted on Standley Lake and its tributaries during the same time period. The sample points for the Standley Lake Raw Water Series are listed in Table 7 and shown on the map in Figure 30. Samples, taken at the points along Clear Creek, were monitored to provide background water quality data for the water that enters Standley Lake and the Lower Clear Creek Ditch. The two wastewater plant effluents were monitored to assess their effect on raw water obtained from Standley Lake. As mentioned above, the Columbine Water Treatment Plant can draw water from the Lower Clear Creek canal as a raw water source and water from Standley Lake can be diverted through a pipeline that runs between the Thornton Water Treatment Plant and the Columbine Plant.

Analyses

The sampling schedule, along with the parameters analyzed, is shown in Table 8. Sampling methods, analytical procedures, and instrumentation are the same as described for the pilot plant program. Refer to Tables 3, 4, and 5, respectively, in Section 6, Pilot Plant, for information. A QA program, previously discussed, was used to ensure accuracy in sampling and analytical procedures. Following is a brief description of the parameters analyzed during the raw water monitoring program.

Inorganic

The samples from both the Raw Water Monitoring Program and the Standley Lake Raw Water Series were analyzed for alkalinity, chlorine residual, hardness, metals, nitrogen species, dissolved oxygen, and pH. In addition, the Standley Lake samples were analyzed for orthophosphate and total phosphorus because of their effect on lakes as nutrients. Nutrient loading affects algal production which then impacts the trophic condition of the lake. The trophic condition of the lake has a great effect on water quality, relating to tastes and odors, chlorine and coagulant demands, and the presence of metals. Consequently, trophic condition significantly affects the overall water treatment process system.

TABLE 7. STANDLEY RAW WATER SERIES SAMPLE POINTS

Designation	Description
CC #1	Clear Creek at Church Ditch
CC #2	Clear Creek at Farmers Highline Canal
CC #3G	Coors Industrial/Golden Municipal Wastewater Plant Effluent
CC #3E	Coors Process Plant Effluent
CC #3F	Clear Creek at Youngfield Road
CC @ LLC	Clear Creek at Lower Clear Creek Ditch
CC #4	Croke Canal at Standley Lake
# 24	Standley Lake Outflow (sample taken at either the Thornton Water Treatment Plant or the City of Westminster's Semper Water Treatment Plant.)

TABLE 8. RAW WATER MONITORING SAMPLING SCHEDULE

Location	Temp.	pH	DO	Turb.	Alk.	Ca	Hard.	TOC	I-TTHM & TTHM-FP	I-TOX & TOX-FP	TKN	NH3, NO3 &NO2	Total Coliform & Coliphage	Metals
Chatfield	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
So. Platte River Upstream	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
So. Platte River Downstream	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Burlington Ditch	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Gravel Lakes	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Well Field	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Clear Creek at Church Ditch	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Clear Creek at FHL	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Coors/Golden WWTP Effluent	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Coors Process Plant Effluent	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Clear Creek at Youngfield	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Clear Creek at LCC	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Croke Canal at Standly	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo
Standley Lake Outflow	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/mo	1/2 wk	1/2 wk	1/6 mo

Alkalinity, hardness, and pH are parameters that are typically monitored in water treatment since they directly affect the coagulation process. The other parameters serve as an indication of the general level of water quality and can give an indication of the extent of exposure to municipal and industrial wastewater in a raw water. Nitrogen species that were analyzed include ammonia, nitrate, nitrite, and TKN. Metals analyses were performed for arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, selenium, silver, and zinc.

Physical

All samples were analyzed for temperature and turbidity, which are parameters that can significantly affect treatment. In addition, the Standley Lake Raw Water Series samples were analyzed for total filterable residue, a parameter for indicating the dissolved solids present in the water supply.

Organic

All samples were analyzed for TOC, TTHM, AND TOX. The Standley Lake samples were also analyzed for chemical oxygen demand (COD). These parameters indicated both general classes of organics and specific information on trihalomethanes that were present in the water supply. In addition, analyses for TTHMFP and TOXFP were conducted. These two parameters are an indication of the quantities of TTHM and TOX that could be formed in each raw water during the water treatment process as a result of reactions with chlorine.

Microbiological

Water supplies are typically monitored for coliform bacteria as an indicator of the microbiological quality. Raw Water Monitoring Program samples for the pilot plant program were analyzed for total coliform. Samples from the Standley Raw Water Series were analyzed for fecal coliform, a more specific indicator for contamination by municipal sewage. Analysis for coliphage began during August, 1984, and the Thornton staff have been developing and refining their techniques. No coliphage results are presented in this report.

RESULTS

Raw data for all of the sources in the Raw Water Monitoring Program and the Standley Lake Raw Water Series have been presented in other reports. The presentation and analysis of data for all of these sources is beyond the scope of this technical report. Only those sources which are currently used, as a raw water supply for the Columbine Water Treatment Plant or are readily available for use in the near future, are being considered in this report. These sources include the Gravel Lakes, the well field, the South Platte River upstream from the Denver Metropolitan Wastewater Disposal District No. 1 (Metro) discharge and the Lower Clear Creek Ditch from the Raw Water Monitoring Program and the Standley Lake outflow from the Standley Lake Raw Water Series.

The analyses performed on the raw water sources of interest in this study include the following parameters: ammonia, nitrite and nitrate, TKN, turbidity, total coliform, TOC, TTHM, and TOX. The data from these analyses are summarized in the following sections. Plots of these parameters versus time for each raw water source are included in Appendix B.

Nitrogen

The nitrogen species analyzed in the raw water sources included ammonia, nitrite, nitrate, and TKN. The nitrite and nitrate data were initially reported as the sum of the two individual species and are presented as such in this report.

Ammonia concentrations in the sources tend to fluctuate between a level less than the detection limit (0.01 mg/L) and 4 mg/L. The source with the lowest ammonia concentrations is the Standley Lake outflow, followed closely by the well field and the Gravel Lakes. The concentration in these sources ranges from less than detectable to 2 mg/L. Early samples from the well field had ammonia concentrations greater than 5 mg/L. These concentrations presumably resulted from operation of wells close to the South Platte River. These wells were taken out of service during the early stages of the study. Clear Creek at the Lower Clear Creek Ditch and the South Platte River upstream of Metro have ammonia concentrations ranging from less than detectable to 4.4 mg/L. Ammonia concentrations in the Gravel Lakes, South Platte River, and Clear Creek sources vary during the year, with higher concentrations occurring during the winter when stream flows and groundwater flows are lower. Higher flows may tend to dilute the ammonia at other times during the year.

The pattern of the nitrite plus nitrate and TKN concentrations in the various sources is the same as that of ammonia. The Standley Lake, well field and Gravel Lakes sources all have nitrite plus nitrate concentrations that average less than 1 mg/L. The Clear Creek and South Platte sources have nitrite plus nitrate concentrations that range from 0.15 to 6.1 mg/L.

TKN measurements in all of the water sources tend to range from 0.05 mg/L to about 6 mg/L. The trends in the measurements over the sampling period tend to follow the ammonia and nitrite plus nitrate levels with the organic nitrogen fraction occurring at levels that are greater than the other forms on several occasions.

Turbidity

Turbidity in all of the sources tended to average between 5 and 25 NTU. The Standley Lake, Clear Creek, and South Platte River sources all had isolated spikes that reached into the 50 to 200 NTU range. The Standley Lake source showed a repeated peak during July and August of each of the three years of the study. This is presumably a delayed response to runoff that occurs in late spring and early summer.

Total Coliform

The total coliform concentrations in the Gravel Lakes and well field sources generally average below 200 organisms/100 mL with some peaks as high as 2,000 organisms/100 mL. The Standley Lake source was only monitored for fecal coliforms with concentrations as high as 1,048 organisms/100 mL. Higher total coliform concentrations are likely. The Lower Clear Creek and South Platte River sources had total coliform concentrations averaging approximately 30,000 organisms/100 mL with peaks as high as 210,000 organisms/100 mL.

Total Organic Carbon

The TOC measurement is an indication of the amount of organic material present in the water source. This is of concern when chlorination is used as the method of disinfection in that chlorinated organics, many of which are carcinogenic, can be formed from reactions between some of this organic matter and chlorine. The total organic carbon concentration in all of the sources normally ranged between 3 and 10 mg/L with isolated peaks up to 58 mg/L. There was no indication of patterns that related to time or flow rate.

Trihalomethanes

All the raw water sources had low concentrations of TTHMs with values typically less than 10 ug/L. Another test used as an indicator of raw water quality, with respect to trihalomethane, is TTHMFP. The purpose of this test is to determine the potential of the raw water to form TTHM during chlorination. Although TTHM actually formed from water treatment chlorination is typically less than the TTHMFP, this parameter provides a useful indication of the tendency for formation. TTHMFP ranged from approximately 100 to 700 ug/l, with the higher levels present during the summer months.

Total Organic Halogen

Trihalomethanes comprise only a portion of the organohalogen compounds. TOX provides an indication of the total concentration of halogens contained in organic compounds present in the raw water. Although some compounds which comprise the TOX have been identified, many have not. TOXFP was also determined to evaluate the effects of chlorination.

TOX concentrations typically ranged from less than the detection limit (1 ug/L) to 100 ug/L, with peaks of approximately 500 ug/L. The Standley Lake source had the lowest TOX concentration, averaging approximately 12 ug/L. TOXFP concentrations ranged from approximately 100 to 1,000 ug/L. Again, the Standley Lake source had the lowest TOXFP concentrations with an average concentration less than 300 ug/L.

SECTION 8

BATCH STUDIES OF CHLORINATION CHARACTERISTICS

GENERAL

Several batch studies were performed to evaluate critical characteristics with respect to disinfection and formation of chlorinated byproducts over a range of chlorination conditions. These studies were intended to supplement the pilot plant work by providing a comparison of different chlorination approaches on the same water sample. As such, the results from these evaluations yielded a direct comparison between these approaches.

METHODS

The batch experiments were performed by withdrawing 250 milliter aliquots of a sample and placing each aliquot in a headspace free bottle with a chlorine solution for a defined period of time. The pH was controlled in the range of 7.5 to 8.0 to match conditions normally encountered in the water distribution system. Temperature was controlled to match that of the finished water as an approximation of conditions found in the distribution system. The methods used for analysis are the same as those described in the program sections of Sections 6 and 7, Pilot Plant and Raw Water Monitoring, respectively.

RESULTS

The general approach used in all batch studies was to evaluate the characteristics of concern at different locations along a breakpoint chlorination curve. Those points located to the left of the classic breakpoint lie within regions where chloramines are the predominant form of total chlorine residual, and those points to the right of the breakpoint occur within the region of domination by free chlorine. Characteristics that were evaluated include the biocidal effectiveness of different methods of chlorination and the formation of chlorinated byproducts, including trihalomethanes, dichloroacetonitrile, TOX, and organic chloramines.

Chlorinated Byproducts

Figure 31 is a typical breakpoint chlorination curve derived for raw water presently used by the City of Thornton. Also shown on this curve are the levels of trihalomethane and total organic halogen formed at different locations on the curve. Although formation is observed to increase with respect to both parameters after the breakpoint is reached, significant formation, especially in the case of total organic halogen, is observed to the left of the breakpoint. These results are consistent with the findings of the pilot plant experiments that indicate significant levels of trihalomethanes and total organic halogen can be formed by chloraminating under conditions where chlorine and ammonia are added separately to the process stream. The observation that significant levels of total organic halogen can be formed to the left of breakpoint raises questions with regard to the identity of the non-trihalomethane component of this parameter and the possible health effects associated with this component.

To determine whether the observations made for Thornton's raw water were unique, samples were obtained from other water bodies within the Denver Metropolitan area to examine their trihalomethane formation characteristics under different chlorination conditions. The basic characteristics of the breakpoint chlorination curve with respect to the formation of trihalomethanes in these samples are shown in Figure 32. With the exception of the sample withdrawn from Barr Lake, ammonium sulfate was added to each aliquot to yield an ammonia concentration of 1 mg/l NH_3-N before the addition of chlorine. This was required to provide sufficient chlorine demand to yield breakpoint chlorination curves comparable to those observed in raw water sources used at the Columbine Water Treatment Plant during the study. Chatfield Reservoir and the South Platte River upstream of Chatfield Reservoir are located within the same natural drainage as the South Platte River source of water for the treatment plant. However, ammonia concentration is much higher in the downstream source used by the City of Thornton. Barr Lake is a reservoir located northeast of the City of Thornton and contains ammonia at a concentration of approximately 1 mg/L. Therefore, ammonium sulfate was not required to achieve levels comparable to sources presently used by Thornton.

The results shown in Figure 32 indicate that although the formation of trihalomethanes is observed to markedly increase after the breakpoint is reached, significant formation also occurs to the left of breakpoint. In some cases, the trihalomethane formation potential with chlorination to the left of breakpoint approaches or exceeds the present drinking water standard of 100 ug/l.

To examine the possible identity of some of the non-trihalomethane components of TOX, experiments were performed to assess the formation of dichloroacetonitrile and organic chloramine. The results of the assessment of the formation of dichloroacetonitrile

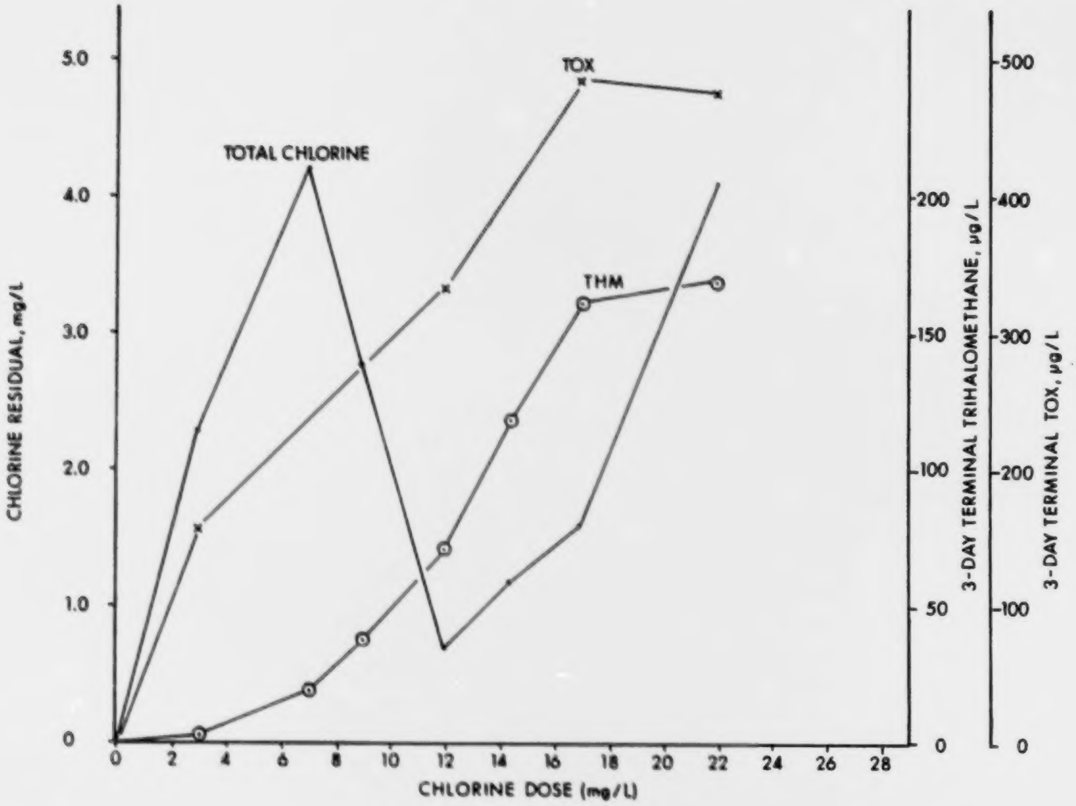


Figure 31. TTHM and TOX formation characteristics along breakpoint curve for Thornton raw water.

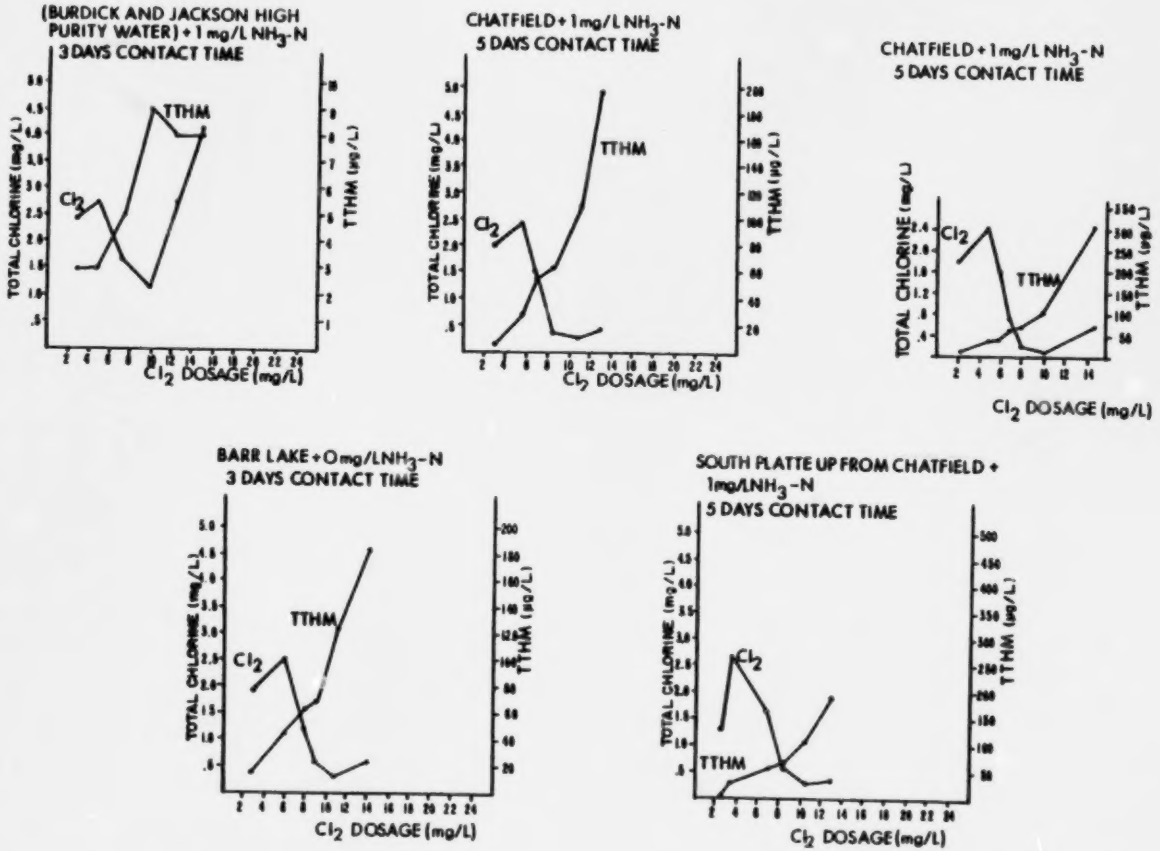


Figure 32. TTHM formation characteristics along breakpoint curve for various Metropolitan Denver raw sources.

are shown in Figure 33. As indicated by this figure, dichloroacetonitrile is formed in a pattern that generally parallels that for the formation of trihalomethanes and occurs at a level of approximately 10 percent of the formation of trihalomethanes.

In the evaluation of organic chloromines, samples were sent to Old Dominion University, Norfolk, Virginia, at the recommendation of the EPA, to perform the breakpoint chlorination experiments in a manner similar to those performed by the City of Thornton. Analyses for organic chloramines were performed by the laboratory at the Old Dominion University using dansyl chloride derivatization as a preparation for analysis using high pressure liquid chormatography. The results indicated that a small quantity of organic chloramine could be formed and that the formation generally tended to parallel the formation of trihalomethane. These results are plotted in Figure 34.

Both organic chloramines and dichloroacetonitrile represent specific non-trihalomethane components of the total organic halogen for which health concerns have been raised. Additionally, the total organic halogen fraction represents a general class of compounds for which health concerns exist. Therefore, it must be noted that disinfection byproducts of concern occur in addition to the trihalomethane species. The fact that the non-trihalomethane component of total organic halogen can occur at appreciable levels both before and after the breakpoint is achieved suggests that concerns for constituents other than trihalomethanes should also be an important consideration in the selection of a disinfection method. While the formation of trihalomethanes can be reduced by chlorination to the left of the breakpoint, the observed formation of significant levels of total organic halogen under these conditions indicates that concerns for disinfection byproducts may not be totally eliminated by such an approach.

Biocidal Effectiveness

A set of experiments were performed to evaluate the bactericidal effectiveness of chlorine at locations along the breakpoint curve that are identified in Figure 35. As identified on this figure, points number 1 and 2 represent the addition of chlorine to form chloramines at points to the left of the breakpoint. Point number 3 represents the addition of chlorine in excess of demand to result in free chlorine residual. Point number 4 represents the addition of chlorine to achieve breakpoint followed by the addition of ammonia to react with the free chlorine to form chloramines. Point number 5 represents the addition of a chloramine solution that is formed prior to addition to the aliquot under investigation. The experiments were performed by adding chlorine as required to yield an initial concentration of 2-1/2 to 3 mg/L. Standard plate count, as shown in Table 9, was used as the basis for evaluating bactericidal effectivenss. Table 9 shows standard plate count

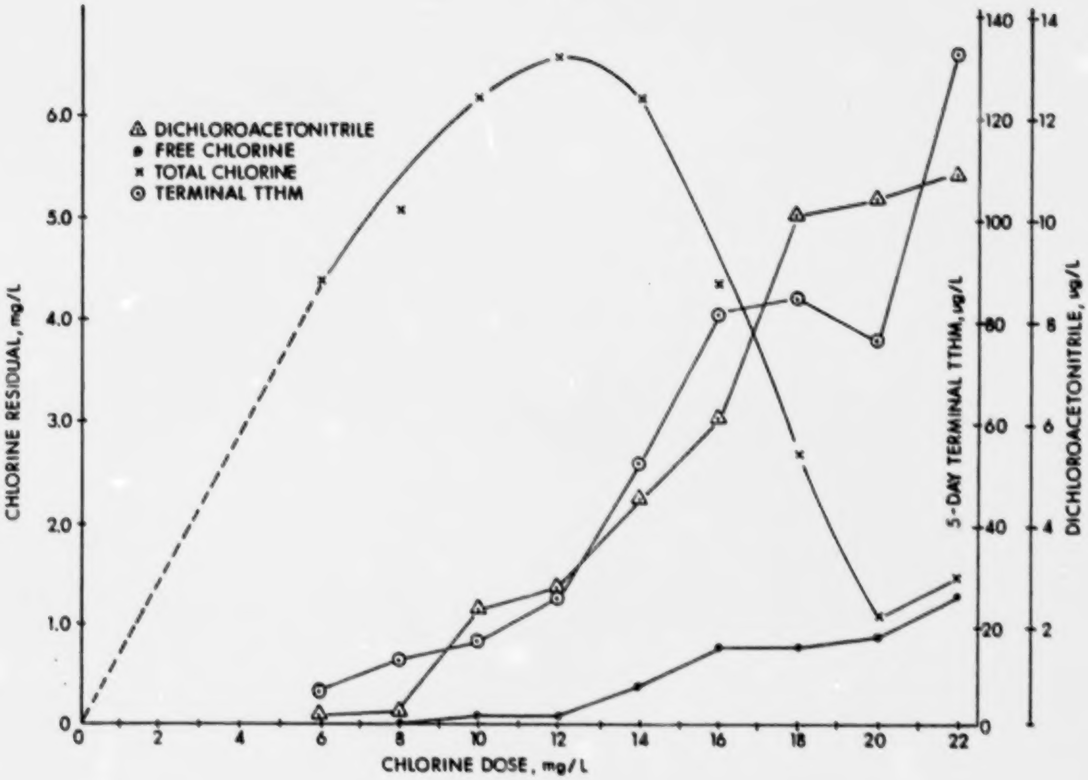


Figure 33. TTHM and DCAN formation characteristics along breakpoint curve for Thornton raw water.

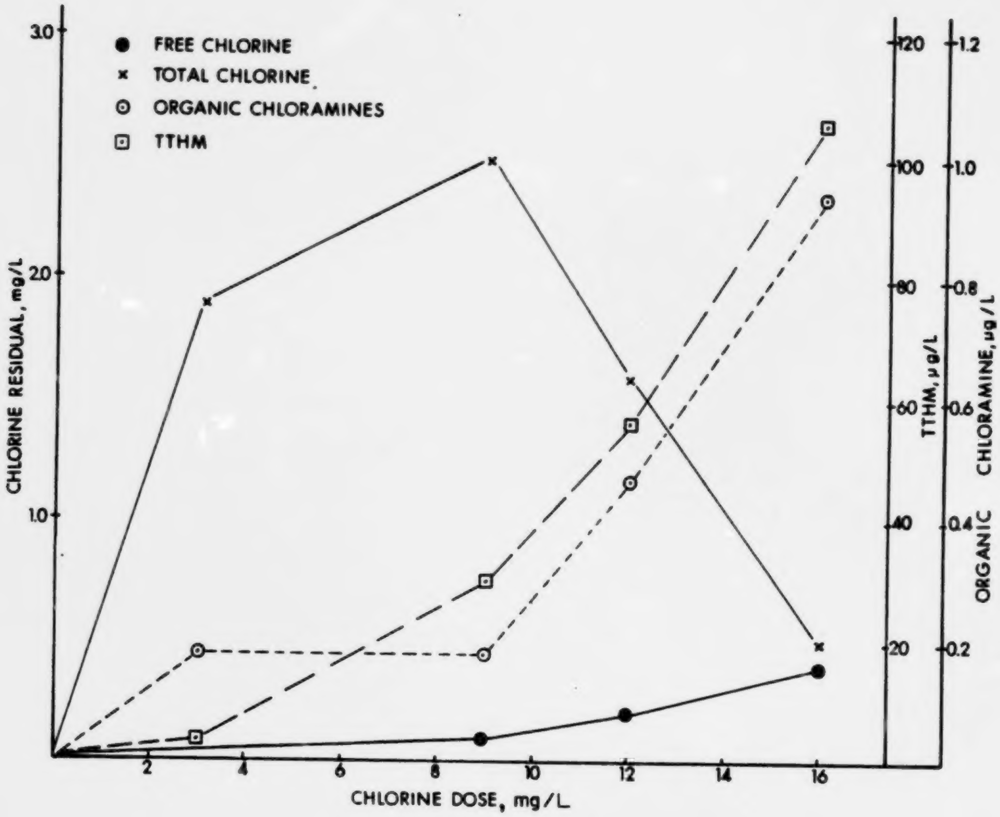


Figure 34. TTHM and organic chloramine formation characteristics along breakpoint curve for Thornton raw water.

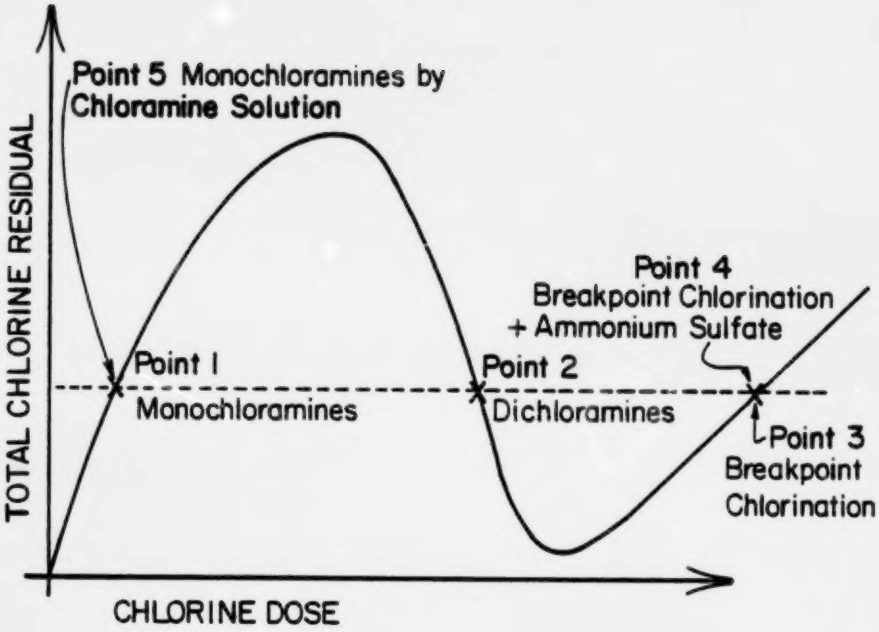


Figure 35. Alternative chlorination schemes on breakpoint curve.

TABLE 9. STANDARD PLATE COUNT OF ALTERNATE CHLORINATION SCHEMES

Raw Water Source	Chlorination Point No.	CFU/mL
Gravel Lakes	1-Monochloramines	TNTC
	2-Dichloramines	16
	3-Free Chlorine	7
	4-Postammoniation	TNTC
	5-Monochloramine Solution	TNTC
South Platte River Downstream from Metro Discharge	1-Monochloramines	250
	2-Dichloramines	22
	3-Free Chlorine	<1
	4-Postammoniation	1
	5-Monochloramine Solution	80

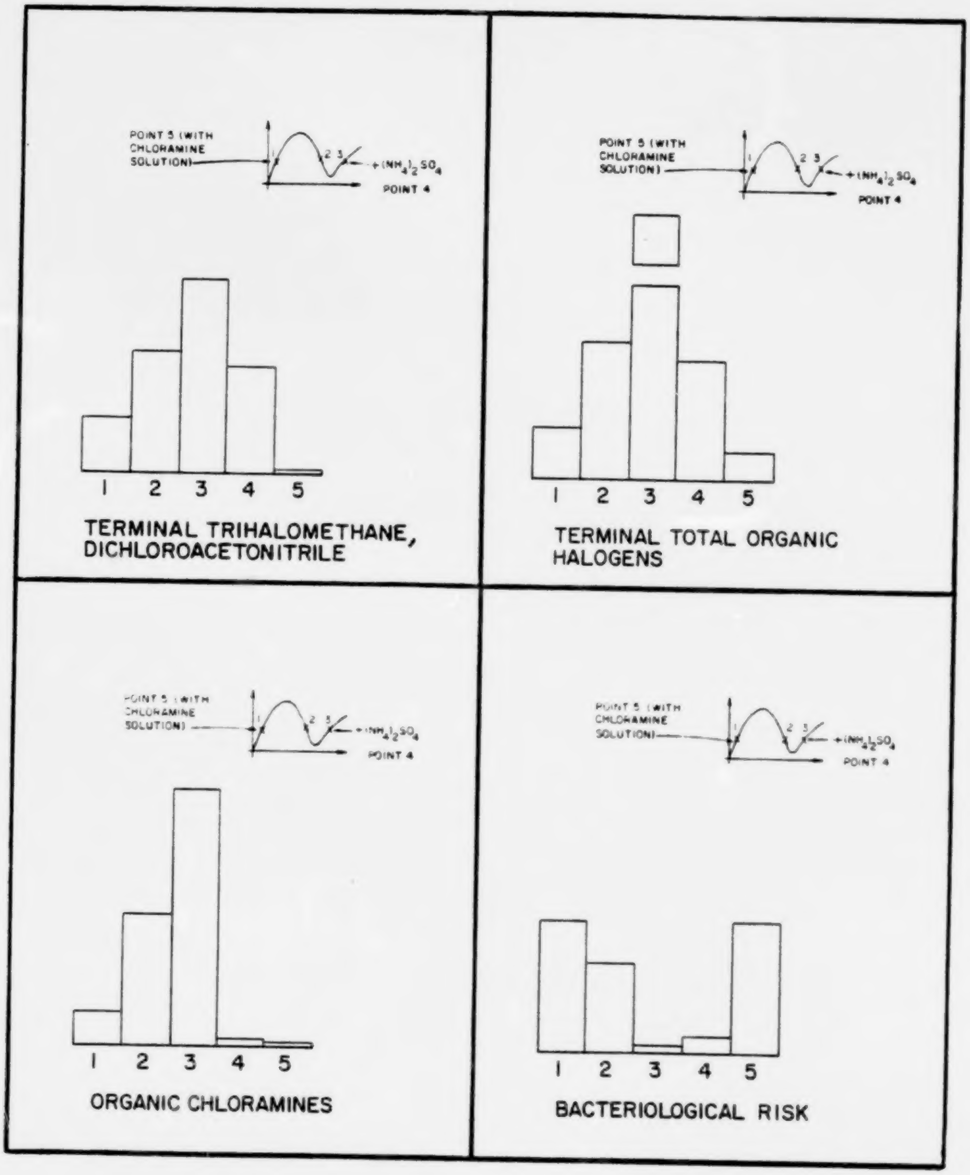
NOTES:

1. TNTC = Too numerous to count
2. Chlorine dosed to achieve a total residual of 2.5 to 3.0 mg/L.
3. Contact time = 180 minutes

data for the 5 chlorination points for two different raw water supplies using a 180 minute contact time. As would be expected, the best results were obtained at point number 3, corresponding to the breakpoint chlorination condition using free chlorine. With the exception of one of the samples taken from the Gravel Lakes, point number 4 was also capable of a relatively high level of reduction in plate count. A relatively high level of reduction was also observed at point number 2, while the lowest level of reduction was observed at points number 1 and 5.

SUMMARY

Overall, the results from the batch experiments can be summarized as shown in Figure 36. The use of breakpoint chlorination to achieve free chlorine at point 3 on the breakpoint curve results in the minimum bacteriological risk, but maximizes the formation of chlorinated byproducts as indicated by trihalomethanes, dichloroacetonitrile, organic chloramines, and total organic halogen. Conversely, the use of chloramine solutions as indicated for point 5, causes the formation of the lowest level of byproducts, but results in the highest level of bacteriological risk. The use of other alternatives for chloramination results in mixed levels of risk for all parameters. It should be noted that, with the exception of the use of chloramine solutions as indicated by point 5, the various chloramination modes result in a significant formation of chlorinated byproducts, in particular total organic halogen.



TERMINAL TRIHALOMETHANE, DICHLOROACETONITRILE

TERMINAL TOTAL ORGANIC HALOGENS

ORGANIC CHLORAMINES

BACTERIOLOGICAL RISK

Figure 36. Comparison of alternative chlorination schemes.

REFERENCES

1. American Water Works Association, Treatment Techniques for Controlling Trihalomethanes in Drinking Water, AWWA (1982).

2. Amy, G.L.; Chadlk, P.A.; King, P.H.; and Cooper, W.J. "Chlorine Utilization During Trihalomethane Formation in the Presence of Ammonia and Bromide," ES&T, Vol. 18, pp. 781 - 786 (October, 1984).

3. Arguello, M.D.; Chriswell, C.D.; Fritz, J.S.; Kissinger, K.L.D.; Lee, K.W.; Richard, J.J.; and Svec, H.J. "Trihalomethanes in Water: A Report on the Occurrence, Seasonal Variation and Concentrations, and Precursors of Trihalomethanes," JAWWA, Volume 71, pp. 504 - 509 (September, 1979).

4. Batchelor, B., and Yang, P. "Removing Trihalomethane Formation Potential by Coagulation with Activated Silica and Cationic Polymer," JAWWA, Vol. 74, pp. 494-498 (September, 1982).

5. Black, A.P. and Christman, R.F. "Chemical Characteristics of Fulvic Acids," JAWWA, Vol. 55, pp. 897 - 912 (July, 1963).

6. Boyce, S.D., and Hornig, J.F. "Reaction Pathways of Trihalomethane Formation from the Halogenation of Dihydroxyaromatic Model Compounds for Humic Acid, ES&T, Volume 17, pp 202 (April, 1983).

7. Brett, R.W., and Claverly, R.A., "A One-Year Survey of Trihalomethane Concentration Changes Within a Distribution System," JAWWA, Vol. 71, pp. 515 - 520 (September, 1979).

8. Briley, K.F., Williams, R.F., Longley, K.E., and Sorber, C.A. "Trihalomethane Production from Algal Precursors," in Water Chlorination: Environmental Impact and Health Effects, R.L. Jolly, W.A. Brungs, and R.B. Cummings, editors, Ann Arbor Science Publishers, Ann Arbor, Michigan (1979).

9. Briley, K.F., Williams, R.F. and Sorber, C.A. "Alternative Water Disinfection Schemes for Reduced Trihalomethane Formation. Volume II. Algae as Precursor for Trihalomethanes in Chlorinated Drinking Water," EPA 600/52-84-005 (1984).

10. Bull, R.J. "Toxicological Problems Associated with Alternative Methods of Disinfection," JAWWA, Vol. 74, pg. 642 (December, 1982).

11. Christman, R.F.; Norwood, D.L.; Millington, D.S.; Johnson, J.D.; and Stevens, A.A. "Identity and Yield of Major Halogenated Products of Aquatic Fulvic Acid Chlorination," ES&T, Vol. 17, pp. 625 - 628 (October, 1983).

12. Coleman, W.E.; Munch, J.W.; Kaylor, W..; Strelcher, R.P.; Ringhand, H.P. and Meier, J.R. "Gas Chromatography/Mass Spectroscopy Analysis of Mutagenic Extracts of Aqueous Chlorinated Humic Acid. A Comparison of the By-products to Drinking Water Contaminants" ES&T, Vol. 18, pp. 614 - 680 (September, 1984).

13. Colthurst, J.M. and Singer, P.C. "Removing Trihalomethane Precursors by Permanganate Oxidation and Manganese Dioxide Adsorption," JAWWA, Vol. 75, pp. 78-83 (February, 1982).

14. Culp, R.L.: Wesner, G.M.; and Culp G.L. Handbook of Advanced Wastewater Treatment, 2nd Edition, Van Nostrand Reinhold Co., New York, NY (1978).

15. Dempsey, B.A.; Ganho, R.M. and O'Melia, C.R., "The Coagulation of Humic Substances by Means of Alumnium Salts," JAWWA, Vol. 76, pp. 141 - 150 (April, 1984).

16. DuRon, B. "Ozone Generation with Ultraviolet Radiation," in Handbook of Oxone Technoloy and Applications. Volume One, Rice, R.G. and Netzer, A. eds., pp. 77 - 84, Ann Arbor Science, Ann Arbor, MI (1982).

17. Englande, A.J. "Water Treatment Process Modifications for Trihalomethane Control and Organic Substances in the Ohio River," Ohio River Vally Water Sanitation Commission, EPA - 600/2-80-028 (March, 1980).

18. EPA, Physical - Chemical Nitrogen Removal (July, 1974).

19. EPA, Treatment of Volatile Organic Compounds in Drinking Water, EPA - 600/8-83-OM (May, 1983).

20. Epton, M.A., and Bechnel, J.F. "Evaluation of Powdered Activated Carbon for Removal of Trace Organics at New Orleans, Louisiana," New Orleans Sewerage and Water Board, EPA -600/52-81-027 (March, 1981).

21. Fernandes, J.B. "THM Precursors Removal from Surface Waters Using Ozone Hydrogen Peroxide Oxidations," Louisiana Water Resources Research Institute Report (July, 1982).

22. Fleischacker, S.J. and Randtke, S.J. "Formation of Organic Chlorine in Public Water Supplies," JAWWA, Vol. 75, pg. 132 (March, 1983).

23. Fuller, P.C. "Status of Research on Ozone Generation by Electrolysis," in the Handbook of Ozone Tecnology and Applications, Volume One, pp. 85 - 104, Ann Arbor Science, Ann Arbor, MI (1982).

24. Glaze, W.H.: Peyton, G.R.; Lin, S.; Hvang, R.Y.; and Burleson, J.L. "Destruction of Pollutants in Water with Ozone in Combination wih Ultraviolet Radiation 2. Trihalomethane Precursors," ES&T, Volume 16, pp. 454 - 458 (August, 1982).

25. Hewes, C.G. and Davison, R.R. "Kinetics of Ozone Decomposition and Reaction with Organics in Water" J.AICHE, Vol. 17, pp. 141 - 147 (January, 1971).

26. Hoehn, R.C., Barnes, D.B., Thompson, B.C., Randall, C.W., Grizzard, T.J. and Shaffler, P.T.B. "Algae as Sources of Trihalomethane Precursors," JAWWA, Volume 72, pp. 334 - 350 (1980).

27. Hoehn, R.C., Dixon, K.L., Malone, J.K., Novak, J.T., and Randall, C.W. "Biologically Induced Variations in Nature and Removability by Alum Treatment of Reservoir Trihalomethane Precursors," Virginia Water Resources Research Center, Bulletin 127 (1983).

28. Hoehn, R.C., Randall, C.W., Malone, J.K., and Dixon, K.L., "Seasonal Variations in Nature and Removability of Reservoir THM Precursors," Virginia Water Resources Research Center, Bulletin 127 (1983).

29. Hoff, J.C. and Geldreich, E.E. "Comparison of the Biocidal Efficiency of Alternative Disinfectants," JAWWA, Vol. 73, pp. 40 - 44 (January, 1981).

30. Hoigne, J. "Mechanisms, Rates and Selectivities of Oxidations of Organic Compounds Initiated by Ozonation of Water," in Handbook of Ozone Technology and Applications, Volume One, Rice, R.G. and Netzer, A. eds., Ann Arbor Science, Ann Arbor, MI (1982).

31. Johnson, J.D., and Jensen, J. "THM and TOX Formation - Routes, Rates and Precursors" presented at AWWA, TTHM Seminar, Las Vegas, NV (June, 1983).

32. Jolley, R.L.: Cumming, R.B.; Lee, N.E.; Lewis, N.R.; Thompson, J.E.; Pitt, W.W.; Denton, N.S. and Hartman, S.J. "Nonvolatile

Organics in Disinfected Wastewater Effluents; Chemical Characterization and Mutagenicity", Oak Ridge National Laboratory, EPA -600/2-82-017 (1982).

33. Kavanaugh, M.C. and Trussell, R.R. "Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water," JAWWA, Vol. 72, pp. 684 - 692 (December, 1980).

34. Kenyon, T.P. "Performance Evaluation for Coupled Trickling Filter-Activated Sludge Nitrification Process," Masters Thesis, University of Colorado (1979).

35. Kool, H.J.; Van Kreijl, C.F.; DeGreet, E; and Van Kranen, H.J. "Presence, Introduction and Removal of Mutagenic Activity During Preparation of Drinking Water in the Netherlands," Envir. Health Persp. Volume 46, pg. 207 (December, 1982).

36. Kringstad, K.P.; deSousa, F.; and Stromberg, L.M. "Studies on the Chlorination of Chlorolignins and Humic Acid," ES&T, Volume 19, pp. 427 - 431 (May, 1985).

37. Kringstad, K.P.; Ljungquist, P.O.: de Sousa, F.; and Stromberg, L.M. "On the Formation of Mutagens in the Chlorination of Humic Acid," ES&T, Volume 17, pp. 553 - 555 (September, 1983).

38. Minear, R.A. and Bird, J.C. "Trihalomethanes: Impact of Bromide Ion Concentration on Yield, Species Distribution, Rate of Formation and Influence of Other Variables" in Jolley, R.L.; Brungs, W.A.; and Cummings, R.B., Eds. Water Chlorination: Environmental Impact and Health Effects, Ann Arbor Science Publ., Ann Arbor, MI, pp. 151 - 160 (1980).

39. Moore, G. S. and Calabrese, E.J. "The Health Effects of Chloramines in Potable Water Supplies: A Literature Review", Journal of Environmental Pathology and Toxicology, Volume 4, pp. 257-263 (1980).

40. National Academy of Science, Drinking Water and Health: (Volume 2) National Academy Press, Washington, D.C. (1980).

41. National Academy of Science, Quality Criteria for Reuse, National Academy Press, Washington, D.C. (1982).

42. Norman, T.S.; Harms, L.L.: and Looyenga, R.N. "The Use of Chloramines to Prevent Trihalomethane Formation," JAWWA, Vol. 72, pp. 176 - 180 (March, 1980).

43. Oliver, B.G. and Shindler, D.B. "Trihalomethanes from the Chlorination of Aquatic Algae," Environ. Sci. Tech., Vol. 14, 1502 - 1505 (1980).

44. Odman, C.S.; Snoeyink, V.L.; O'Connor, J.T.; and Taras, M.J. Removing Trace Organics from Drinking Water Using Activated Carbon and Polymeric Adsorbents," Iowa State University, EPA - 600/52-81-077, 078, 079 (July, 1981).

45. Rav-Acha, C. "The Reactions of Chlorine Dioxide with Organic Materials and Their Health Effects," Water Res., Vol. 18, pp. 1329 - 1341 (November, 1984).

46. Rice, I.M. and Bolding, M.E. "An Alternative Solution to the THM Problem," Water/Engin. and Man., Vol. 128, pp. 59 - 60, 65 - 66 (May, 1981).

47. Rook, J.J. "Haloforms in Drinking Water," JAWWA, Volume 68, pp. 168 - 172 (March, 1976).

48. Scully, F.E.; Yung, J.P.; Mazina, K.; and Daniel, F.B. "Derivatization of Organic and Inorganic N-Chloramines for High-Performance Liquid Chromatographic Analysis of Chlorinated Water," ES&T, Volume 18, pp. 787 - 792 (October, 1984).

49. Singer, P.C.; Borchardt, N.H.; and Colthurst, J.M. "The Effects of Permanganate Pretreatment on Trihalomethane Formation," JAWWA, Vol. 72, pp. 573 - 578 (October, 1980).

50. Stevens, A.A.; Slocum, C.J.; Seeger, D.R.; and Robeck, G.G. "Chlorination of Organics in Drinking Water," in Jolley, R.L., ed. Water Chlorination: Environmental Impact and Health Effects, Vol. I, Ann Arbor Science Publ., Ann Arbor, MI, pp. 77 - 104 (1978).

51. Symons, J.H.; Stevens, A.A.; Clark, R.M.; Geldreich, E.E.; and Love, O.T. "Removing Trihalomethanes from Drinking Water," Water/Engin. and Man., Vol. 128, pg. 50 (July, 1981).

52. Veenstra, J.N. and Schnoor, J.L. "Seasonal Variations in Trihalomethane Levels in an Iowa River Water Supply," JAWWA, Volume 72, 583-590 (1980).

53. Voss, K.J. Votapka, T.; and Bricker, C. "Prechlorination Treatment of Water to Reduce Chloroform Levels" Water Res., Volume 14, pp. 921 - 926 (July, 1980).

54. Wetzel, R.G. Limnology, 2nd Ed., Saunders College Publishing, New York (1983).

55. White, G.C. Handbook of Chlorination, Van Nostrand Reinhold, New York (1972).

56. Young, J.S. and Singer, P.C. "Chloroform Formation in Public Water Supplies: A Case Study," JAWWA, Volume 71, pp. 87 - 95 (February, 1979).

57. Zoeteman, B.C.; Hrubec, J.; deGreef E.; and Kool, H.J. "Mutagenic Activity Associated With By-Products of Drinking Water Disinfection by Chlorine, Chlorine Dioxide, Ozone and UV-Irradiation" Environ. Health Persp., Volume 46, pp. 197 - 205 (1982).

APPENDIX A

EVALUATIONS OF CRITICAL EXPERIMENTAL PARAMETERS

Several studies were performed to evaluate the effect of critical experimental parameters on the formation of trihalomethanes. Parameters that were found to have a significant effect were temperature, time of exposure, and chlorine dose. The effect of temperature was evaluated over a range of chlorine doses in parallel batch experiments at 11°C and 20°C, respectively. The results of this evaluation, as shown in Figure A-1, indicate that a temperature effect is observed, especially at the higher chlorine doses. Therefore, temperature was controlled throughout the pilot plant program when determining formation of trihalomethanes. To accomplish this, the samples were submerged in the clearwell reservoir during the storage period to maintain a temperature representative of the distribution system.

The effect of time of chlorine contact is indicated by Figure A-2 in which terminal trihalomethane is shown as a function of chlorine dose beyond the breakpoint. As shown by these results, some of the reaction for formation of trihalomethane occurs within the first hour of contact, however, the reaction is observed to continue over a period of several days. A small difference is observed between results for three days and five days of contact, indicating that the reaction neared completion. Subsequently, a five day contact period was used for most of the evaluations of potential to form trihalomethanes. In the case of some batch experiments, a three day contact time was used.

During the initial operation of the pilot plant, a number of apparent anomalies were observed with respect to the data for trihalomethane formation. An investigation of the underlying factors that cause these anomalies, indicated that the trihalomethane formation characteristic of the water under investigation was more strongly influenced by chlorine dose than had been anticipated based on general observations in literature. This is illustrated by the results shown in Figure A-3, comparing the formation of trihalomethanes in raw water used by the City of Cincinnati, Ohio to that used by the City of Thornton. As indicated by these results, water used by the City of Cincinnati is much less sensitive to chlorine dose. Measurements of chlorine

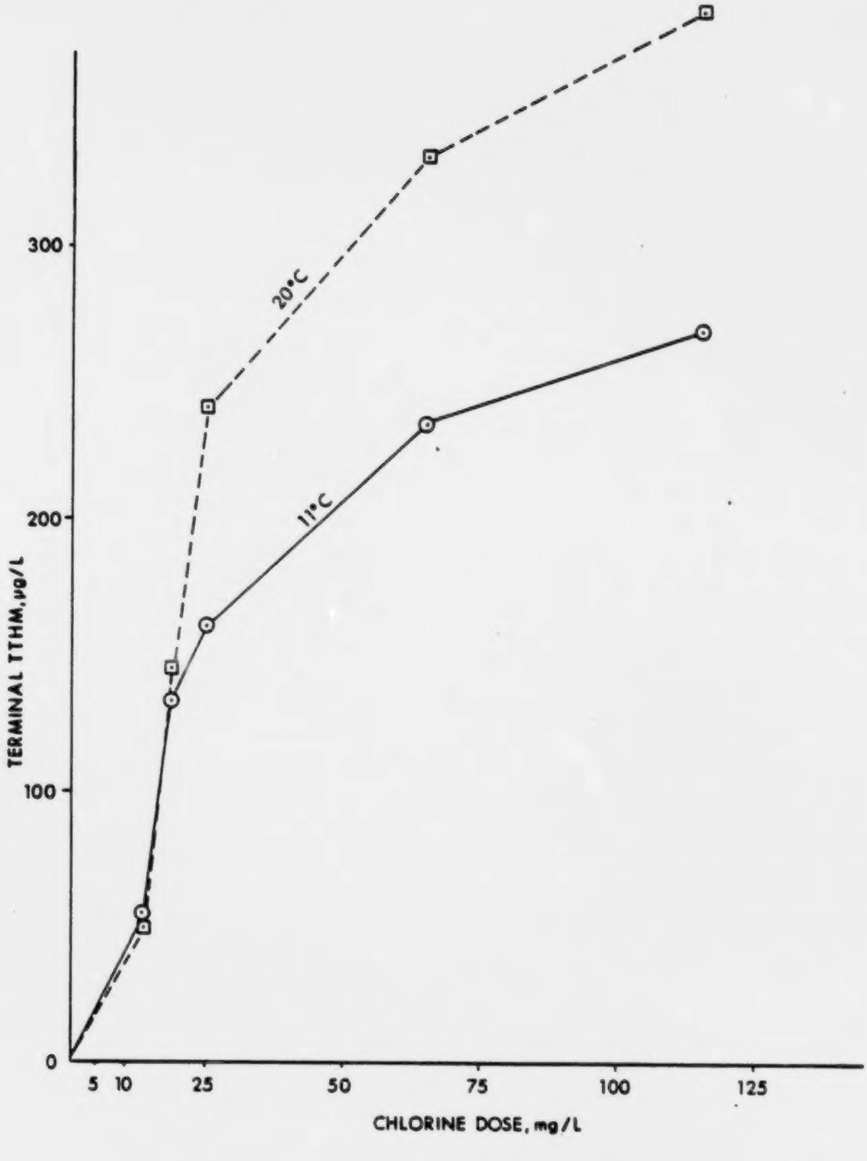


Figure A-1. Effect of temperature on TTHM formation.

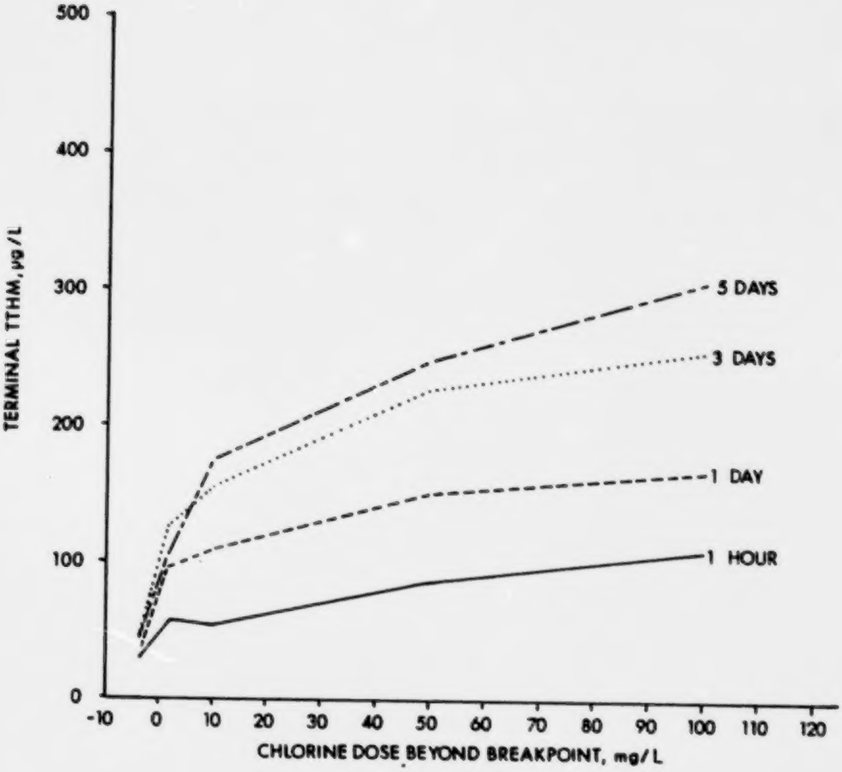


Figure A-2. Effect of contact time on TTHM formation.

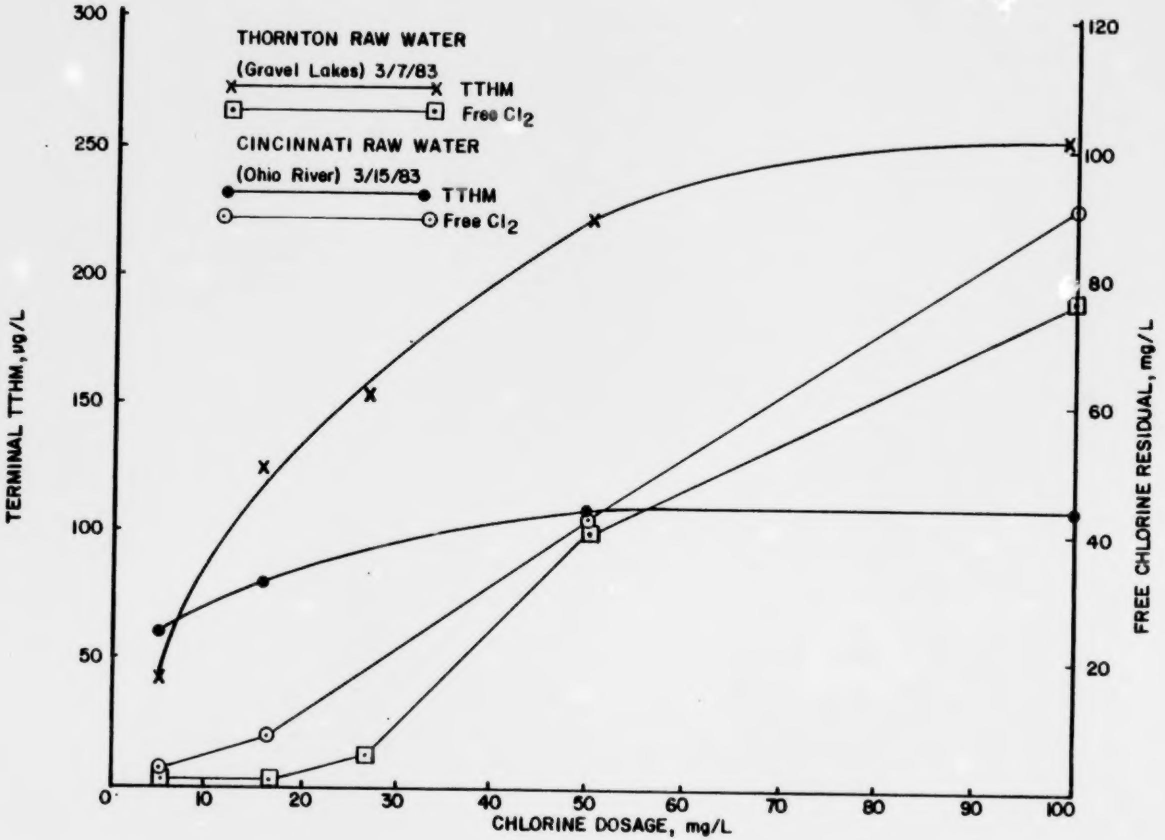


Figure A-3. Effect of chlorine dose on TTHM formation for surface waters.

residual performed during these experiments indicate that the breakpoint had been reached in all cases. In addition, experiments were controlled with respect to pH and temperature. As will be discussed further in the text, the effect of chlorine dose on the formation of trihalomethane was observed to occur throughout the study, on a generally seasonal basis. To account for the possible effects of the dose, dose control procedures were implemented for evaluation of the trihalomethane formation potential.

Although not specifically investigated, pH is a parameter that is particularly important for reactions that occur in aqueous systems, and has specifically been observed to have an affect on the formation of trihalomethanes. Therefore, pH was maintained in a region of 7.5 to 8.0, to compare to the pH of Thornton's finished water.

APPENDIX B

RAW WATER MONITORING RESULTS

Plots of the ammonia, nitrite and nitrate, TKN, turbidity, TOC, TTHM, TOX, and total coliform data versus time are shown for each of five raw water sources in Figures C-1 through C-40. The sources include the Gravel Lakes, well field, South Platte River upstream from Metro, Lower Clear Creek Ditch, and Standley Lake outflow.

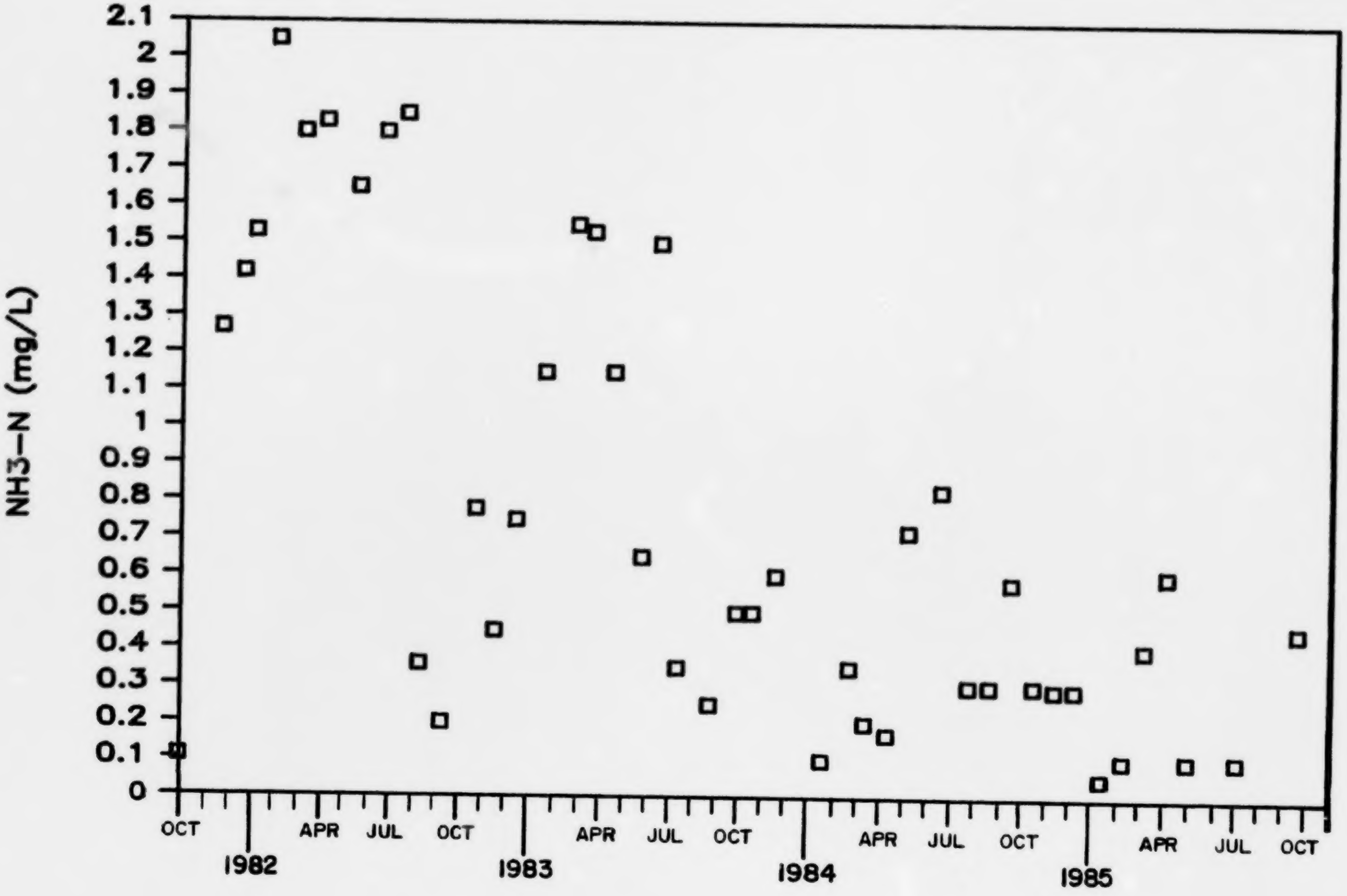


Figure B-1. Ammonia concentration in the Gravel Lakes.

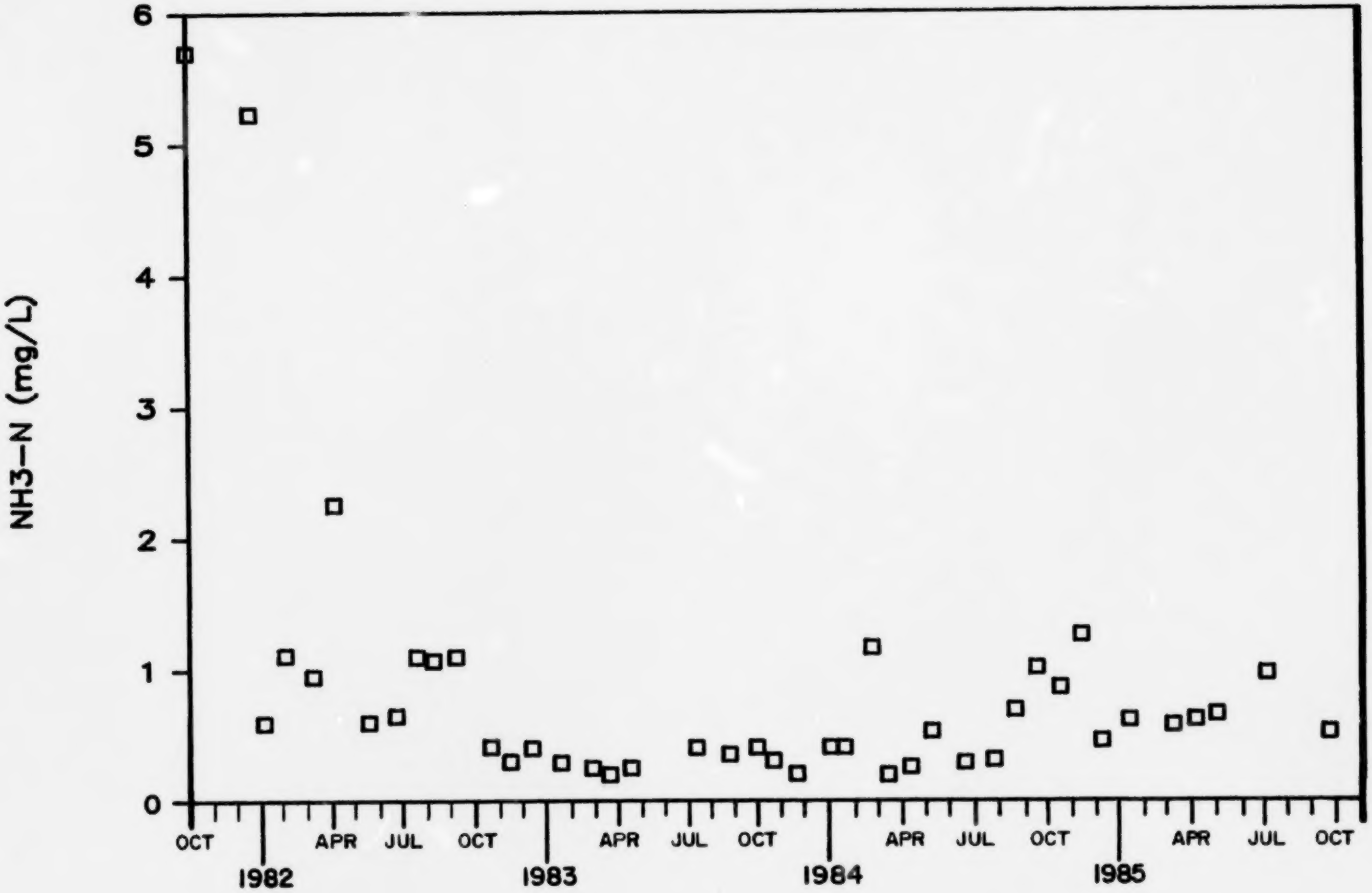


Figure B-2. Ammonia concentration in the Well Field.

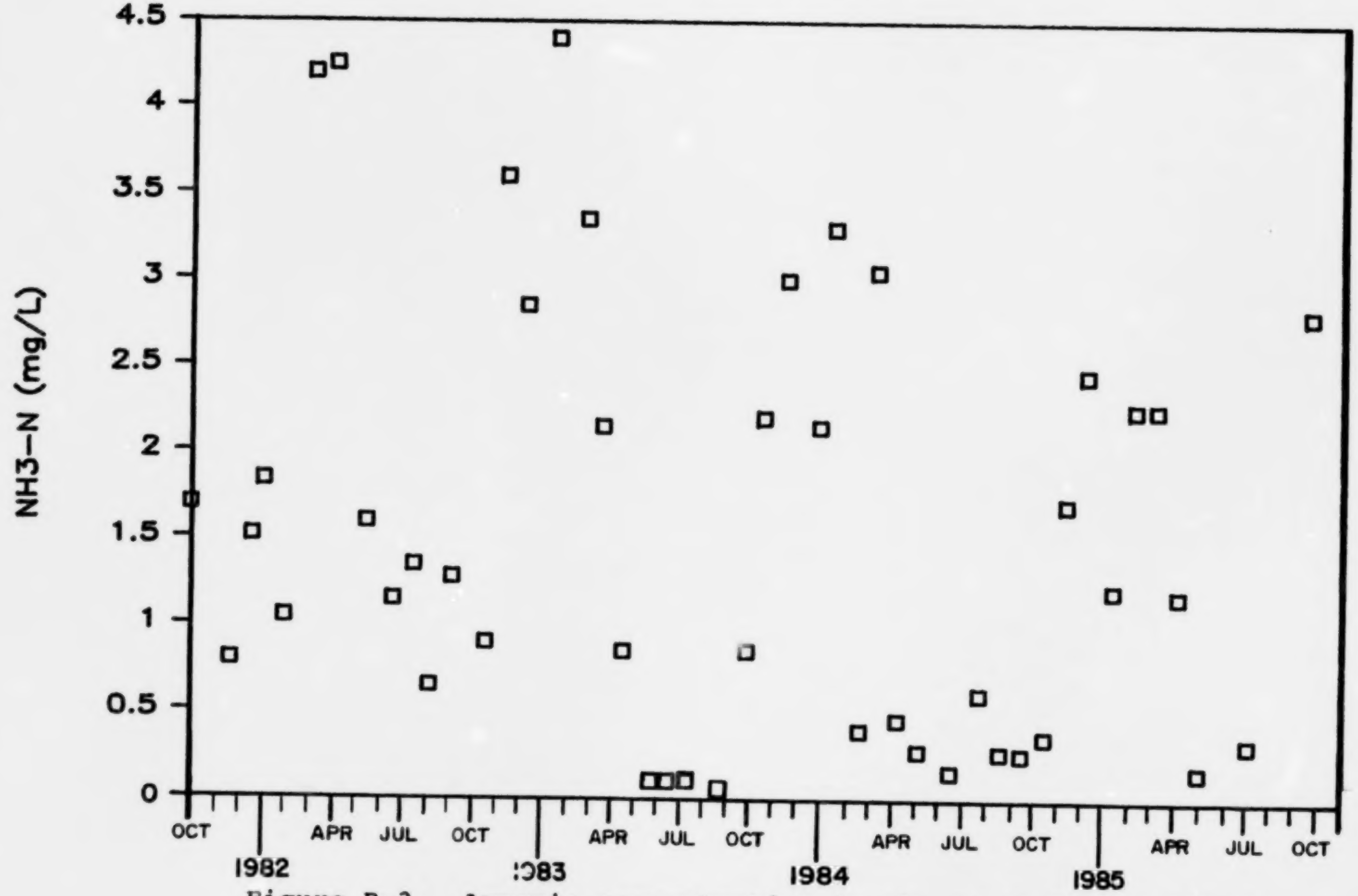


Figure B-3. Ammonia concentration in the South Platte River upstream of the Metro discharge point.

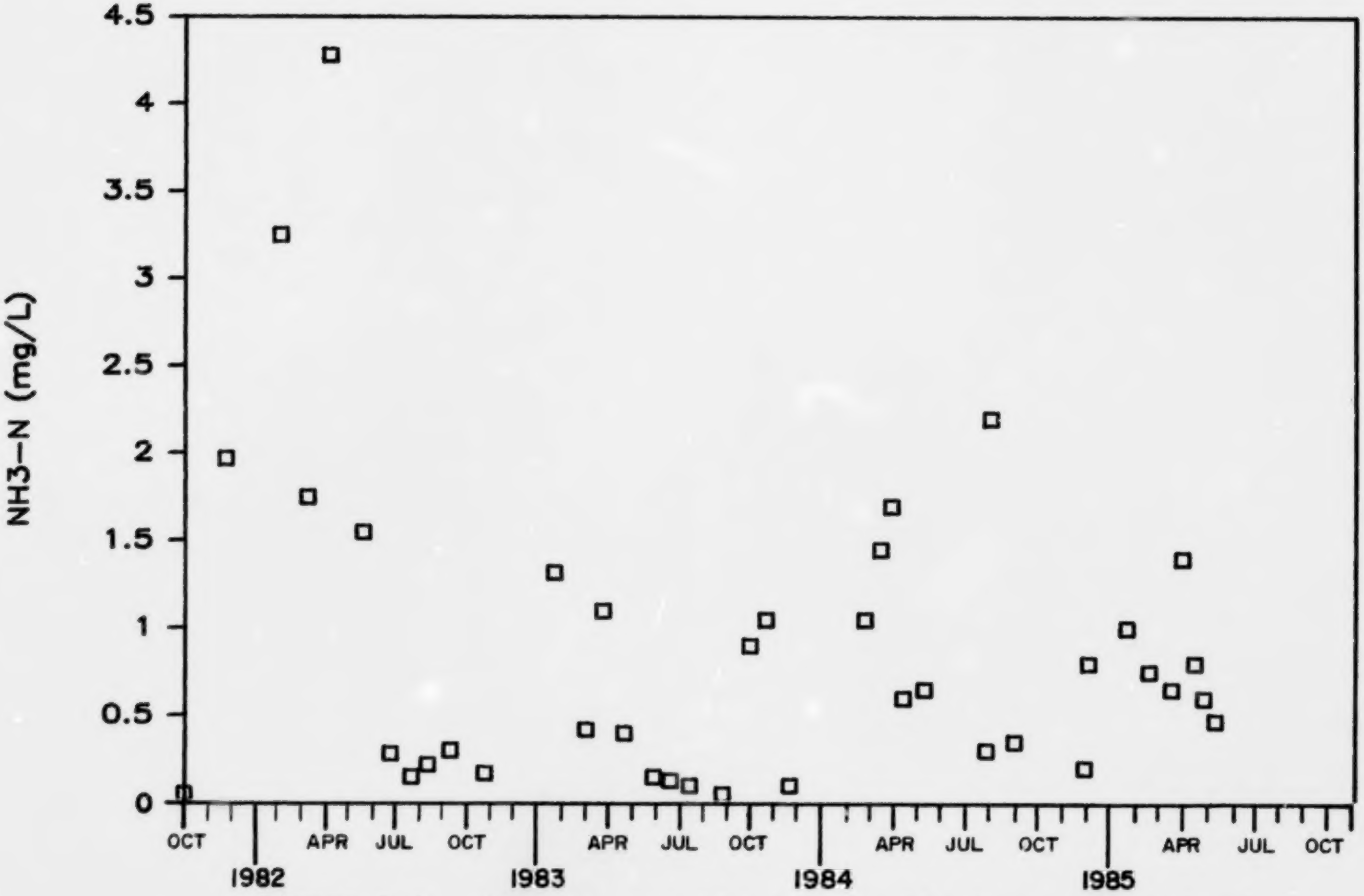


Figure B-4. Ammonia concentration in the Lower Clear Creek ditch.

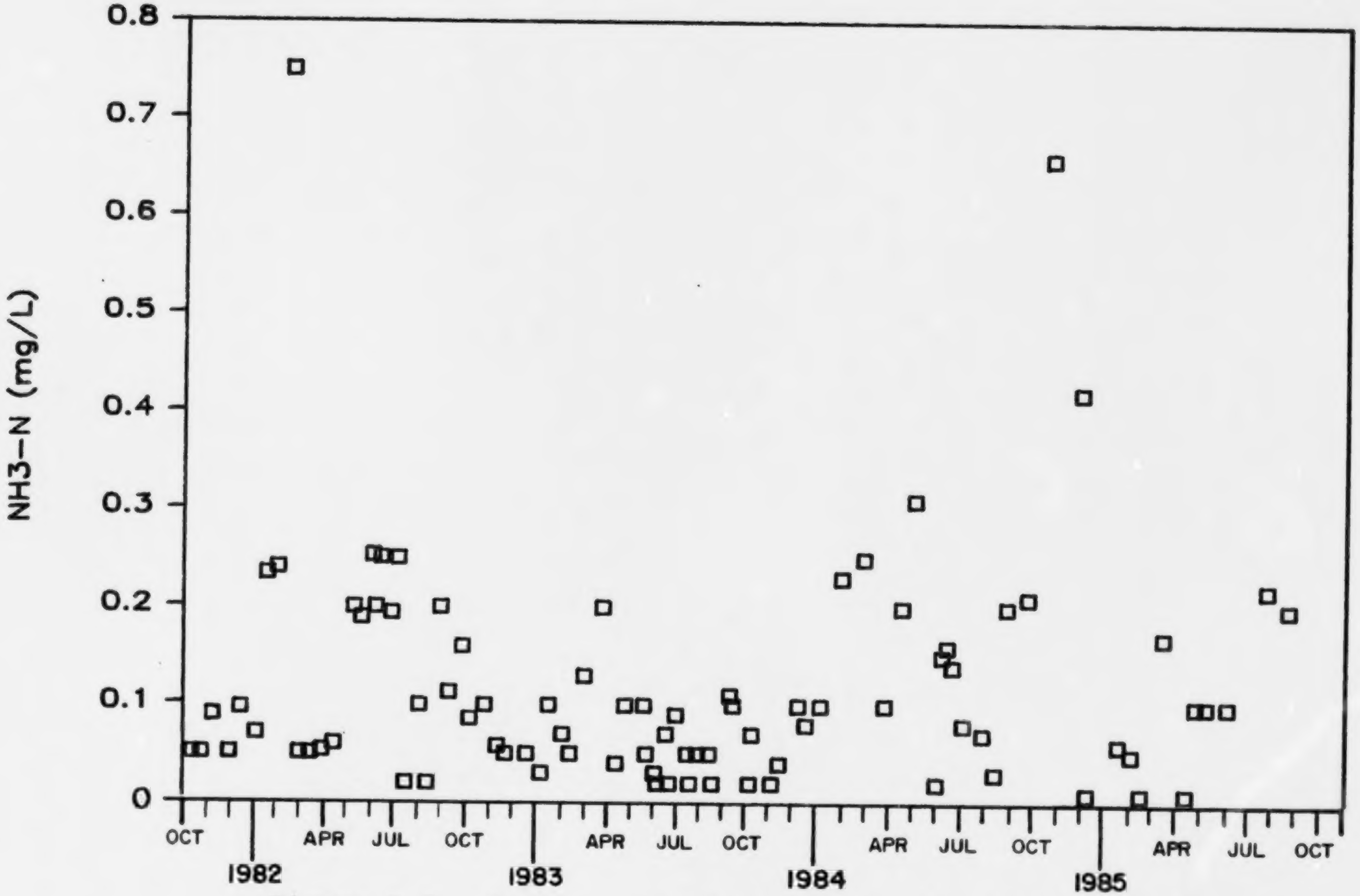


Figure B-5. Ammonia concentration in the Standley Lake outflow.

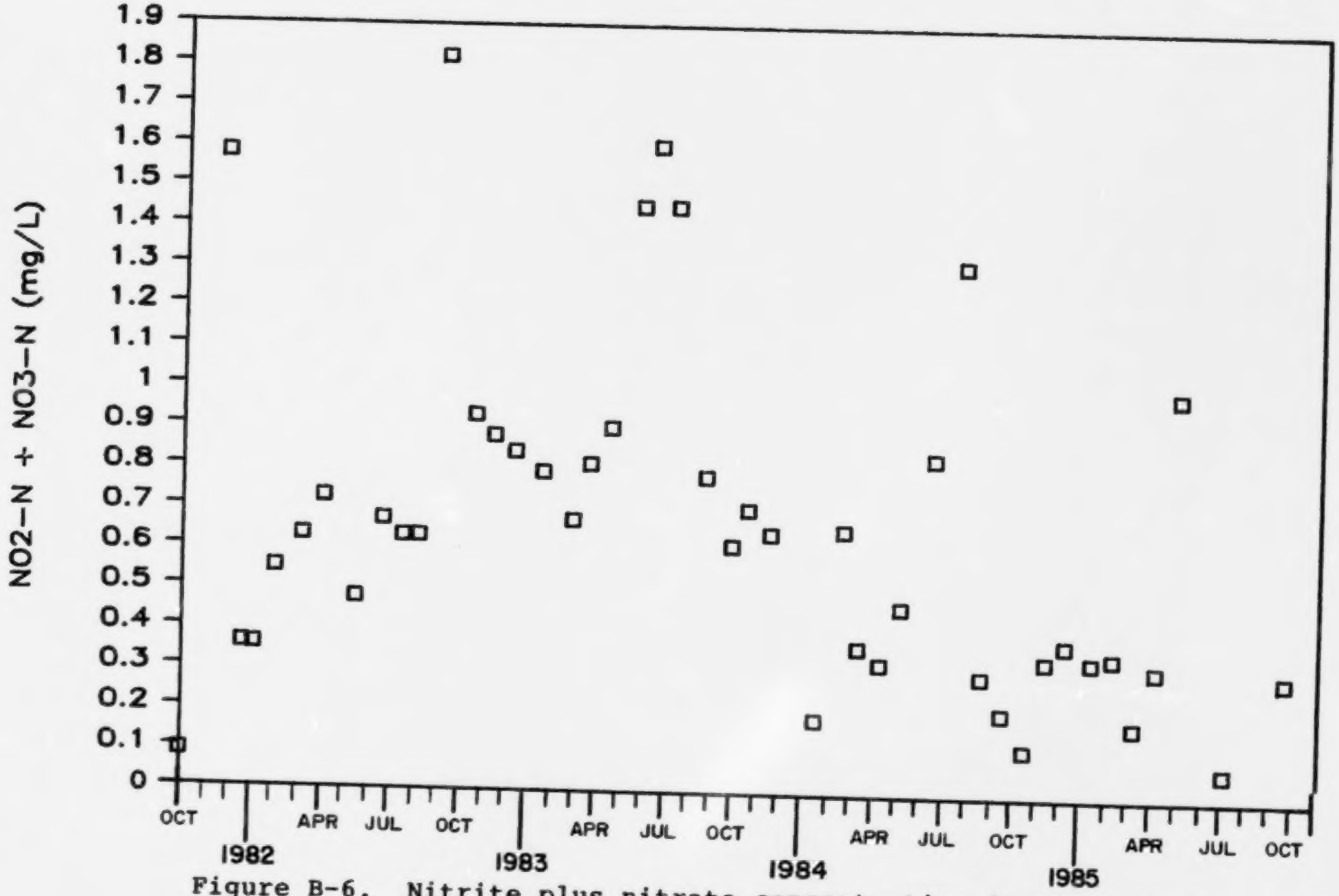


Figure B-6. Nitrite plus nitrate concentration in the Gravel Lakes.

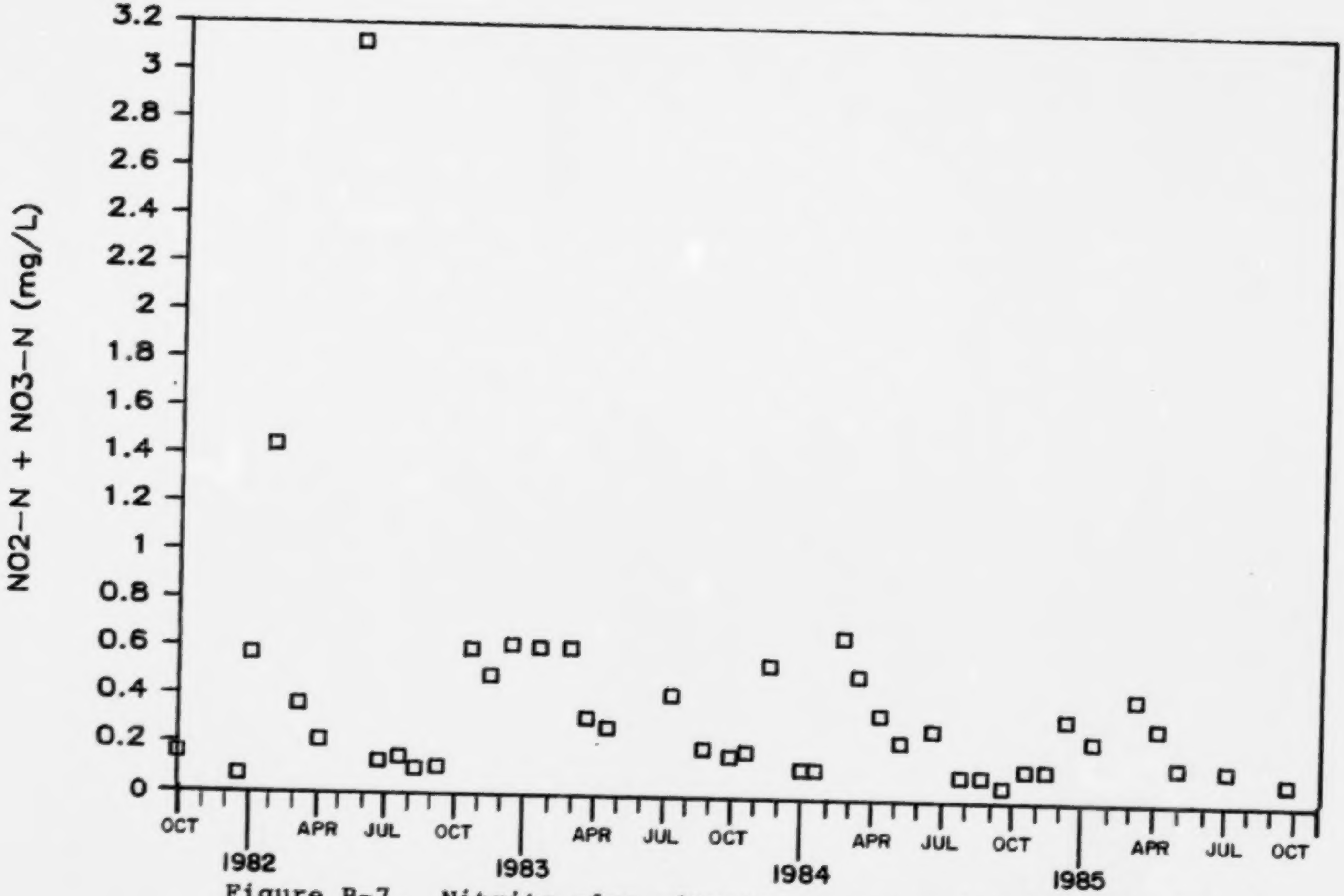


Figure B-7. Nitrite plus nitrate concentration in the Well Field.

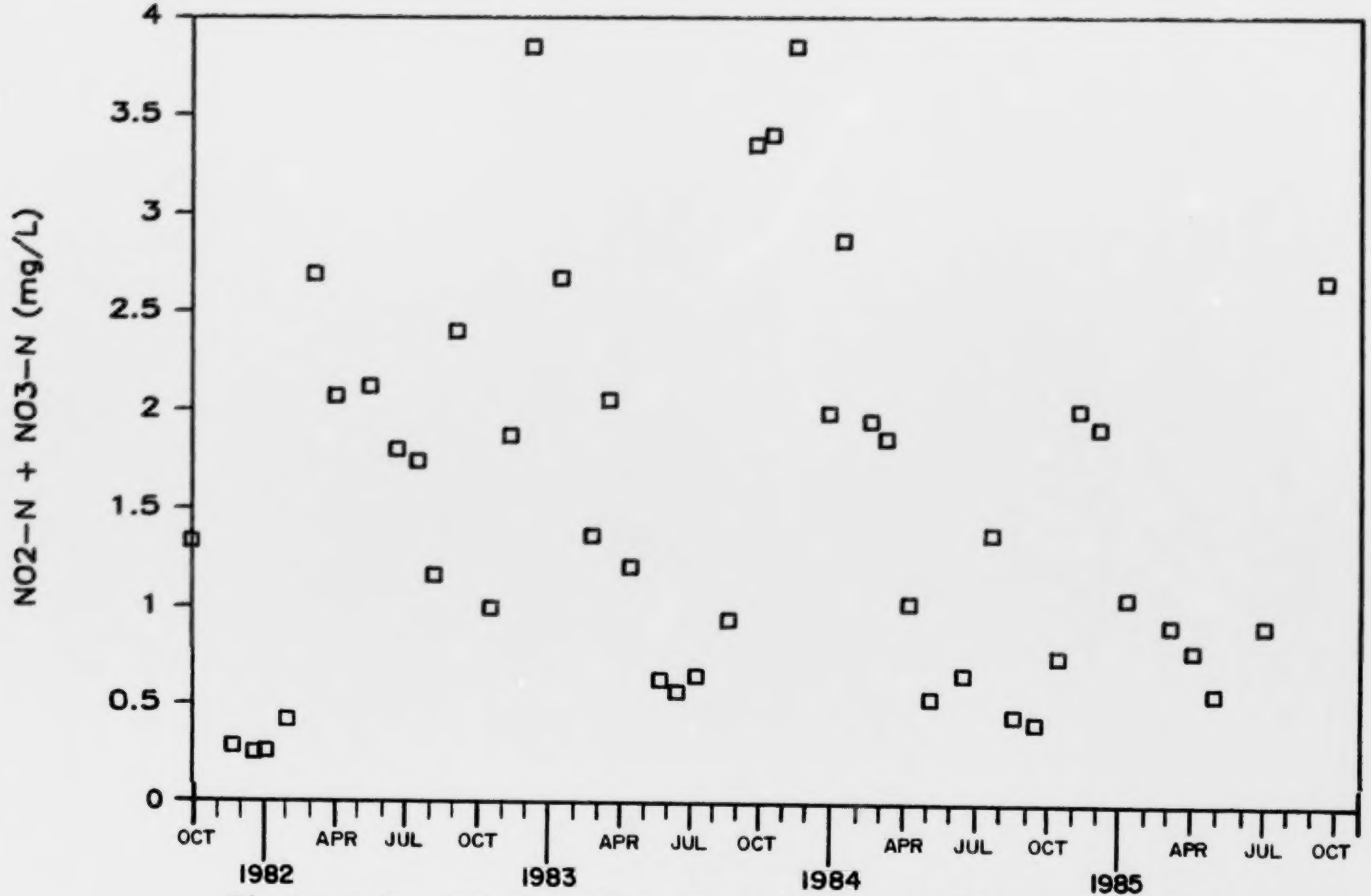


Figure B-8. Nitrite plus nitrate concentration in the South Platte River upstream of the Metro discharge point.

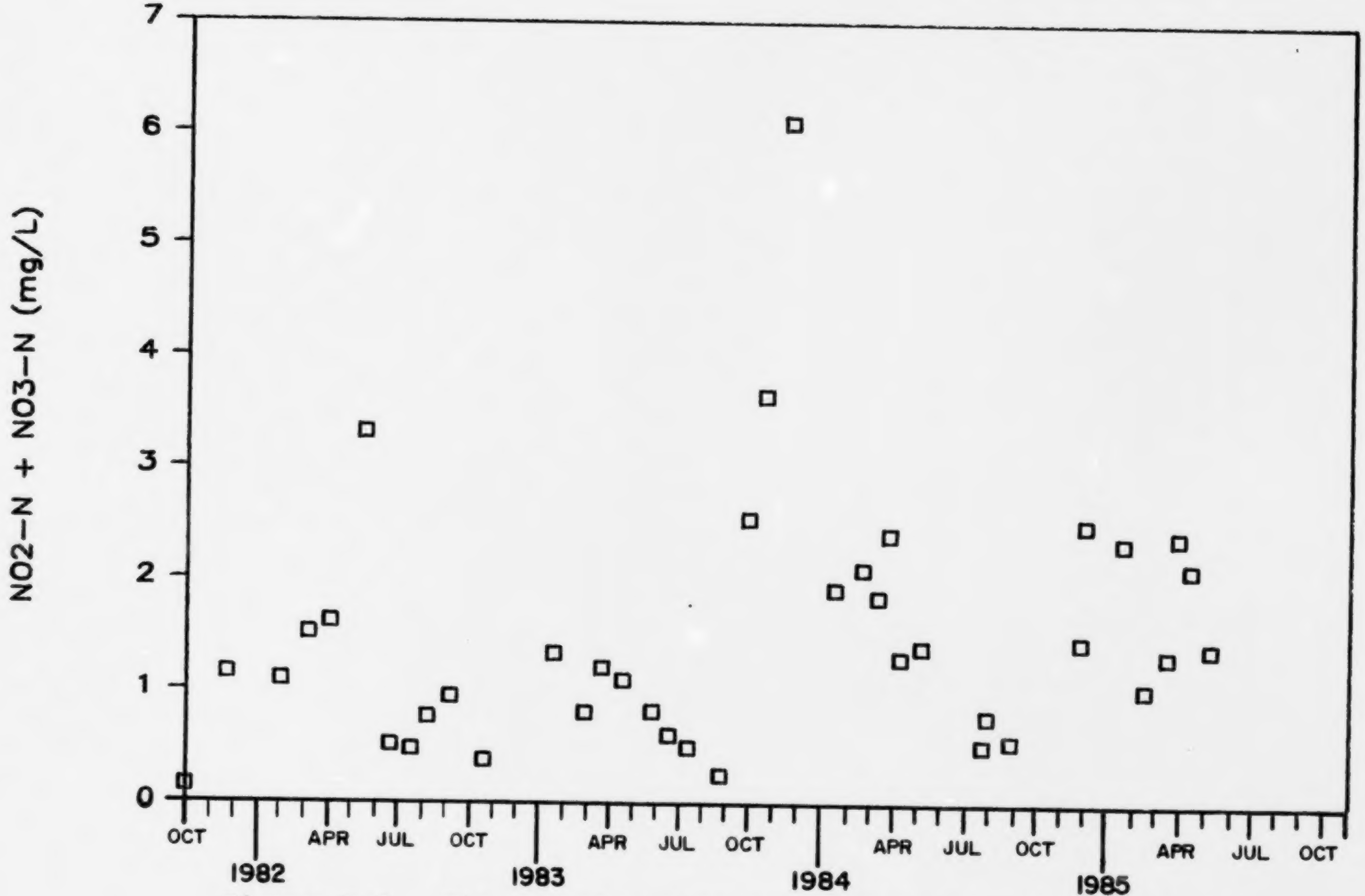


Figure B-9. Nitrite plus nitrate concentration in the Lower Clear Creek ditch.

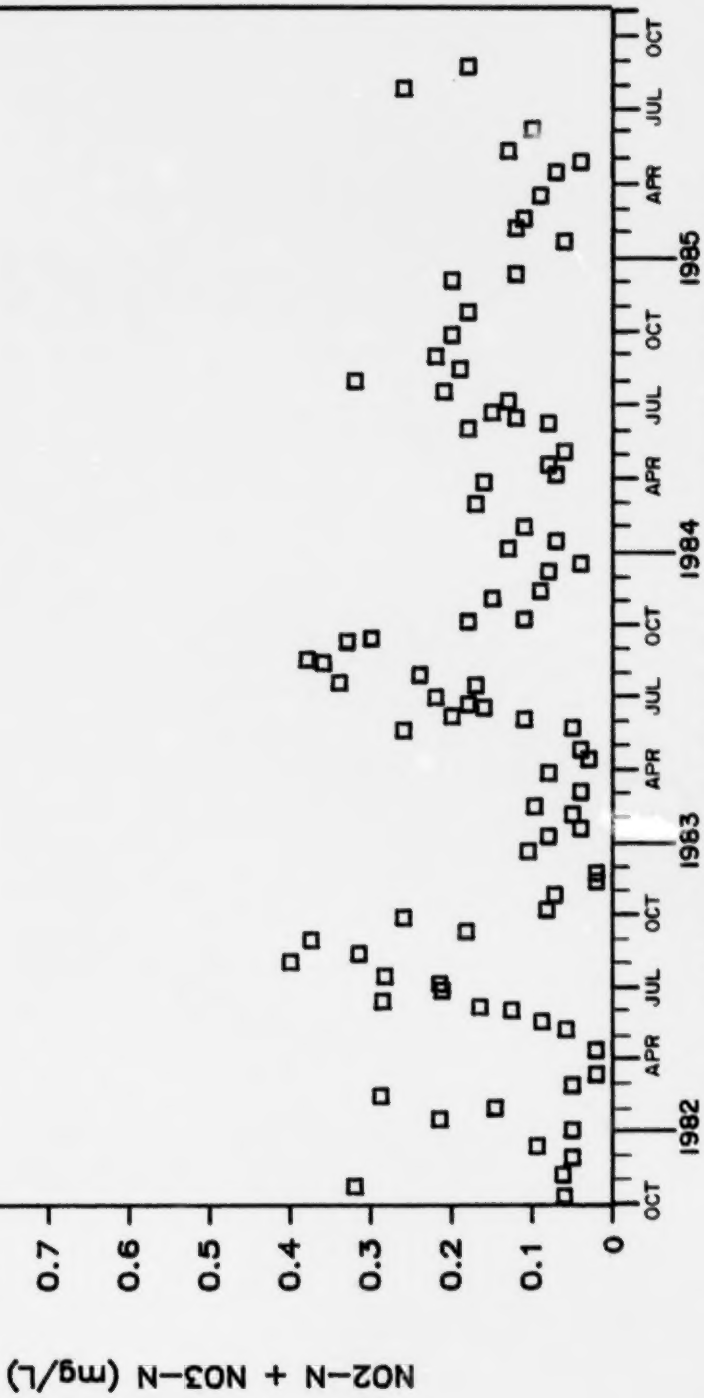


Figure B-10. Nitrite plus nitrate concentration in the Standley Lake outflow.

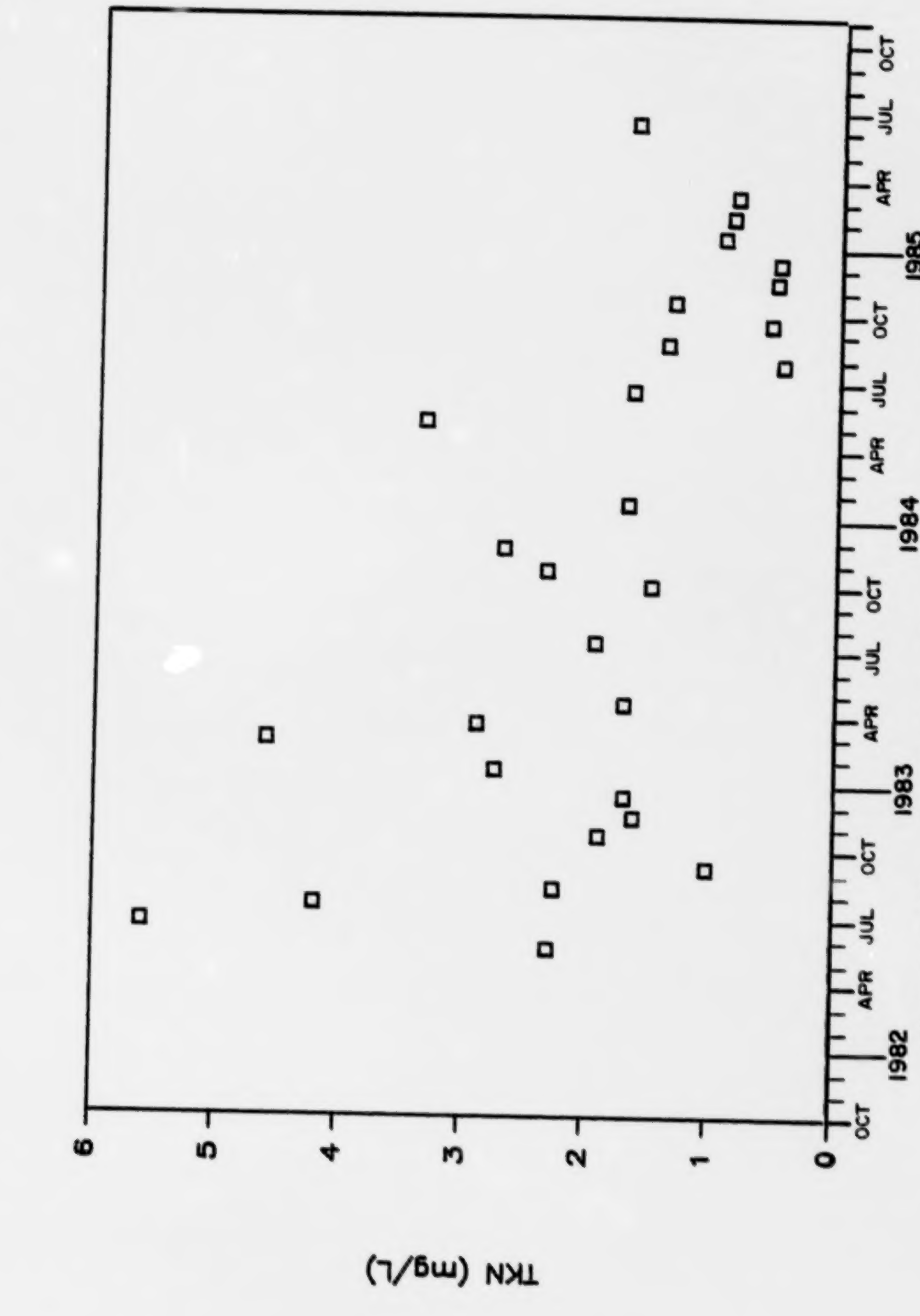


Figure B-11. Total Kjeldahl nitrogen concentration in the Gravel Lakes.

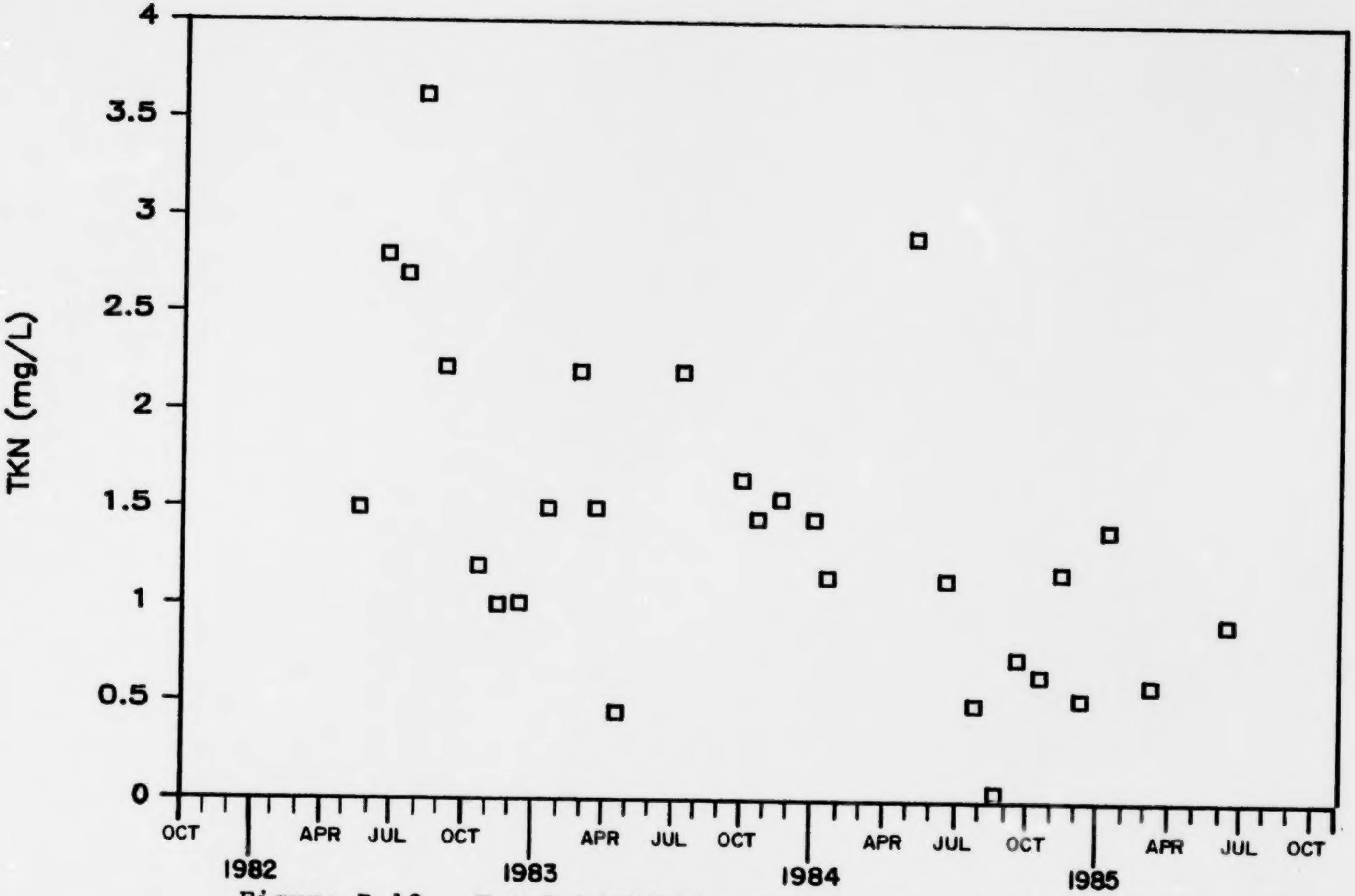


Figure B-12. Total Kjeldahl nitrogen concentration in the Well Field.

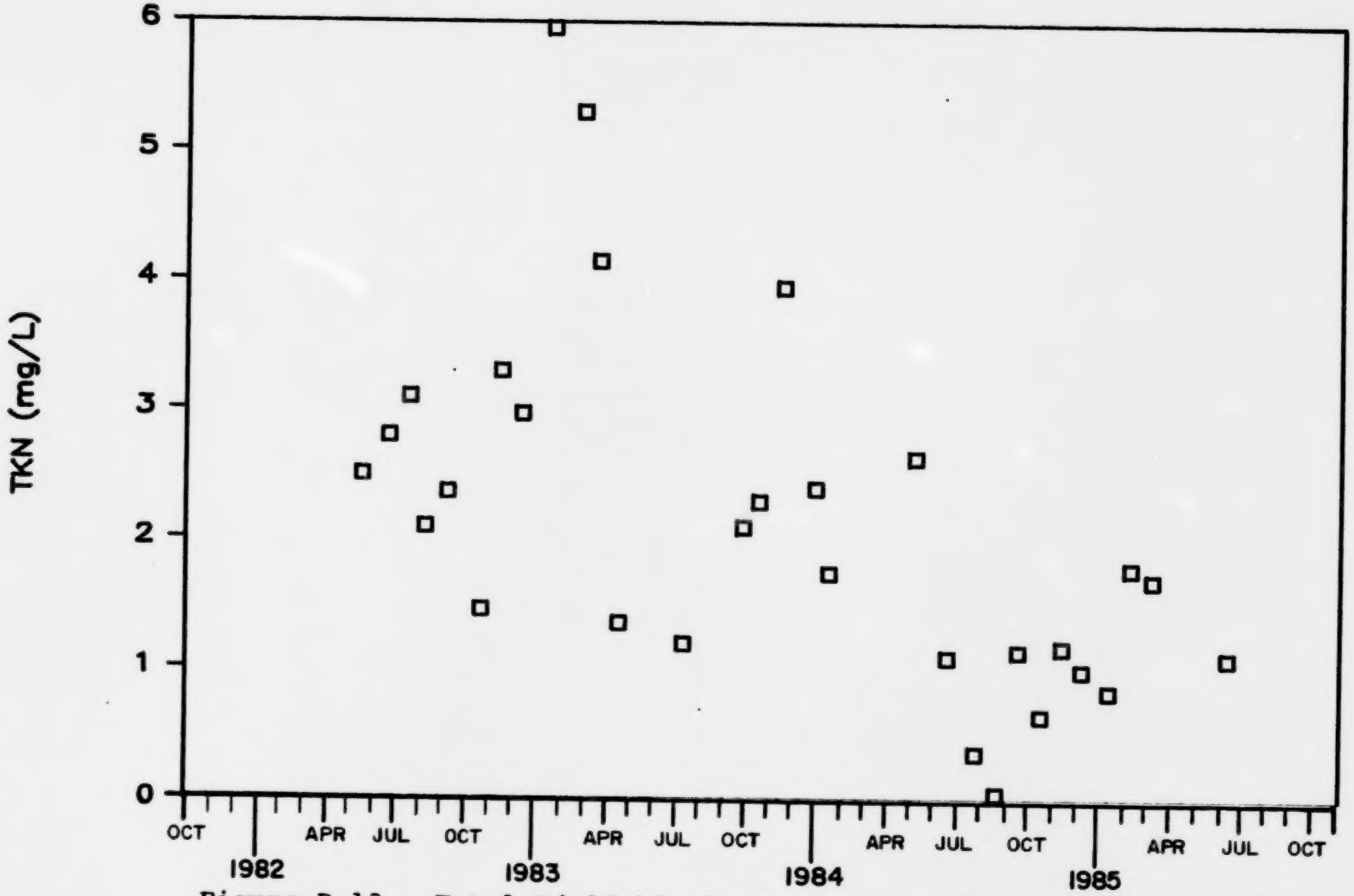


Figure B-13. Total Kjeldahl nitrogen concentration in the South Platte River upstream of the Metro discharge.

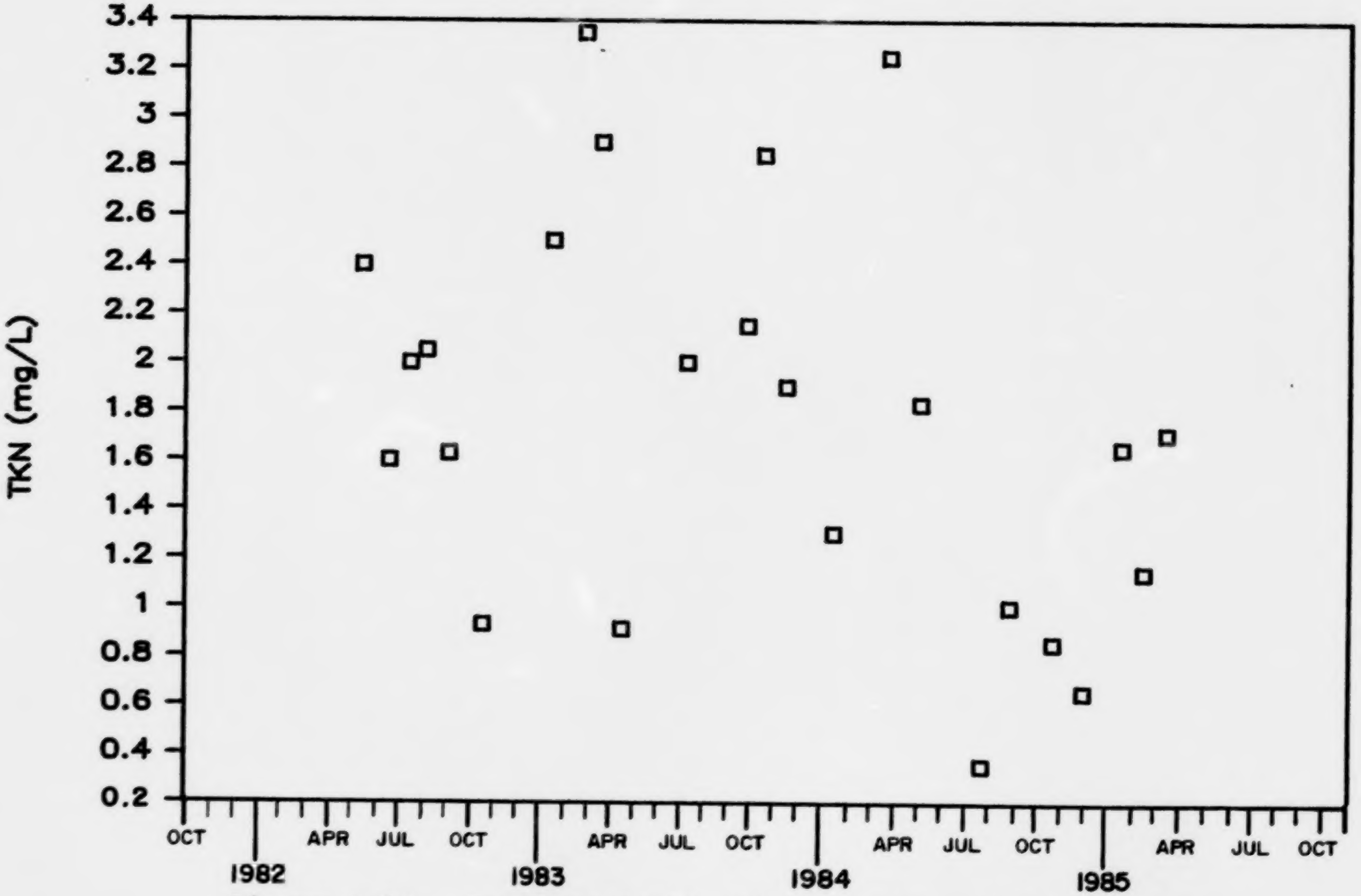


Figure B-14. Total Kjeldahl nitrogen concentration in the Lower Clear Creek ditch.

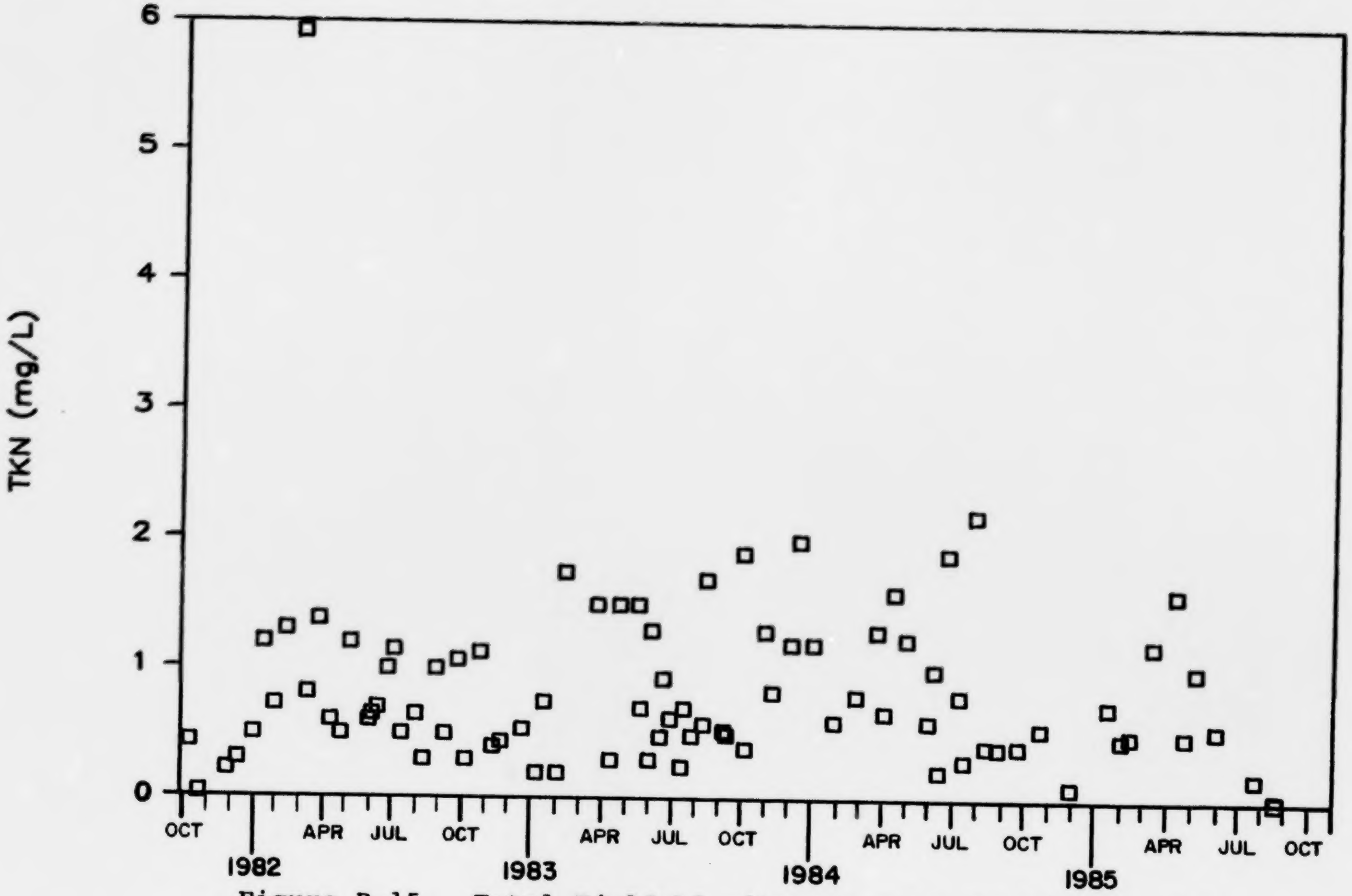


Figure B-15. Total Kjeldahl nitrogen concentration in the Standley Lake outflow.

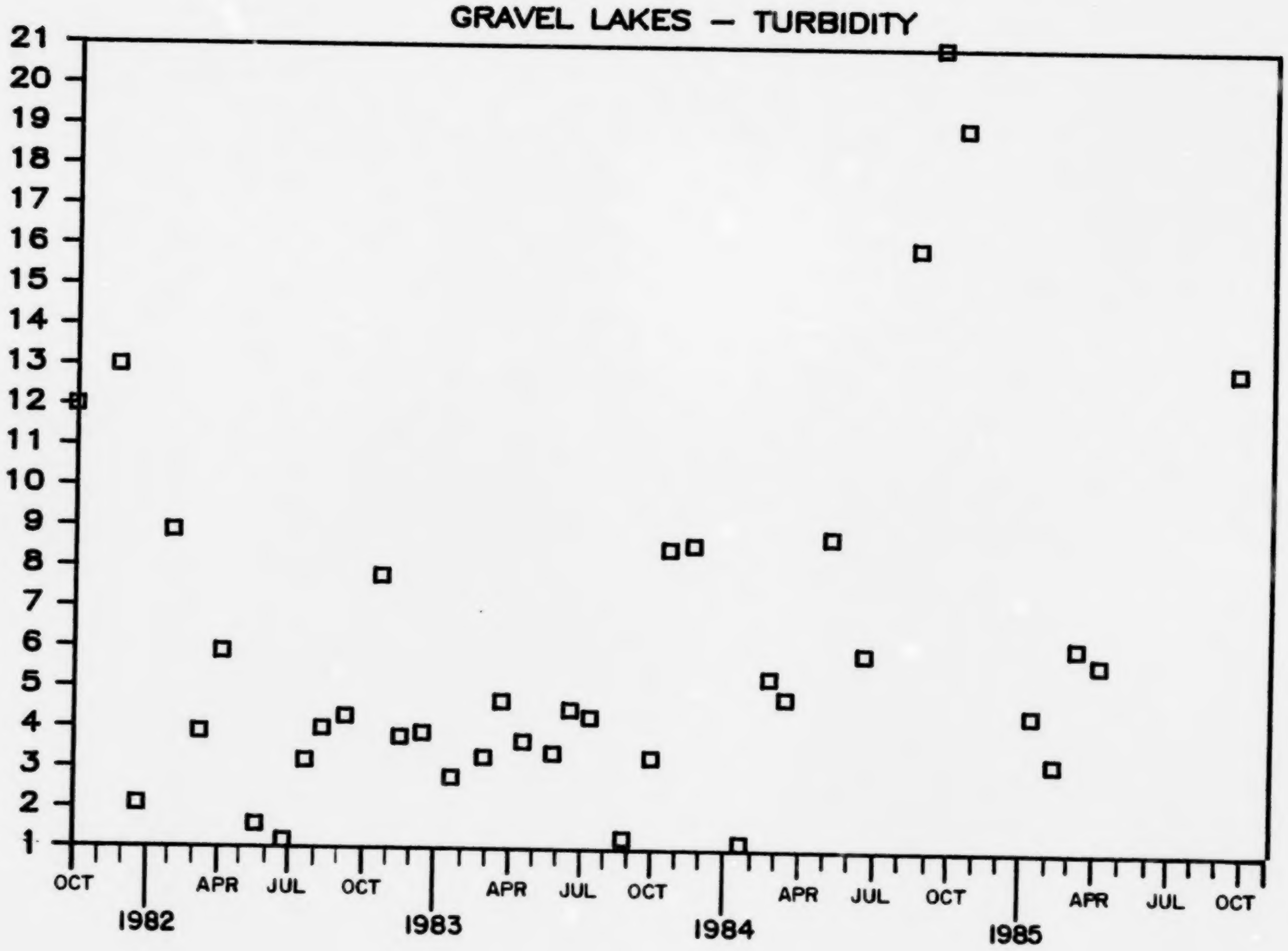


Figure B-16. Turbidity in the Gravel Lakes.

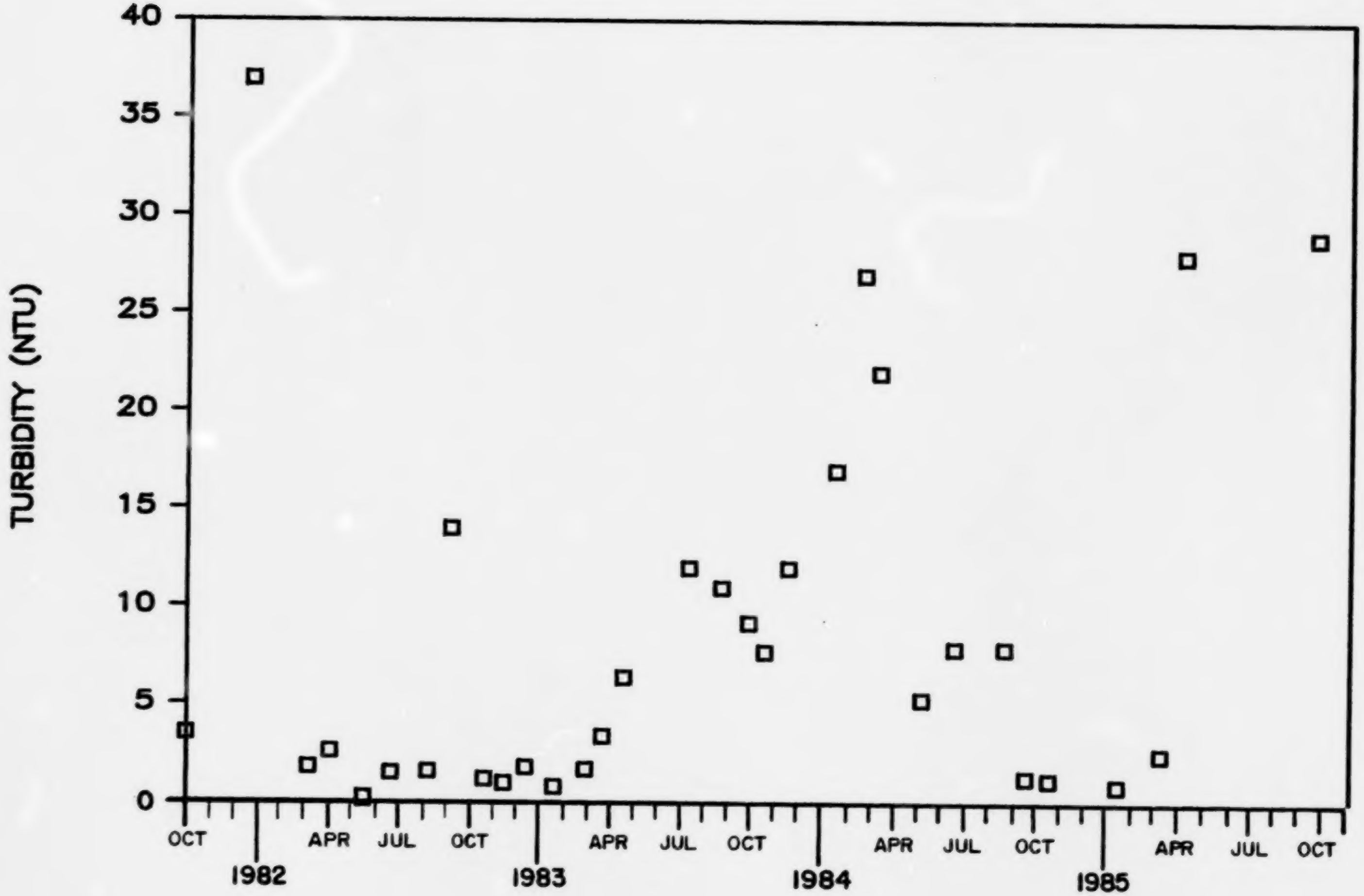


Figure B-17. Turbidity in the Well Field.

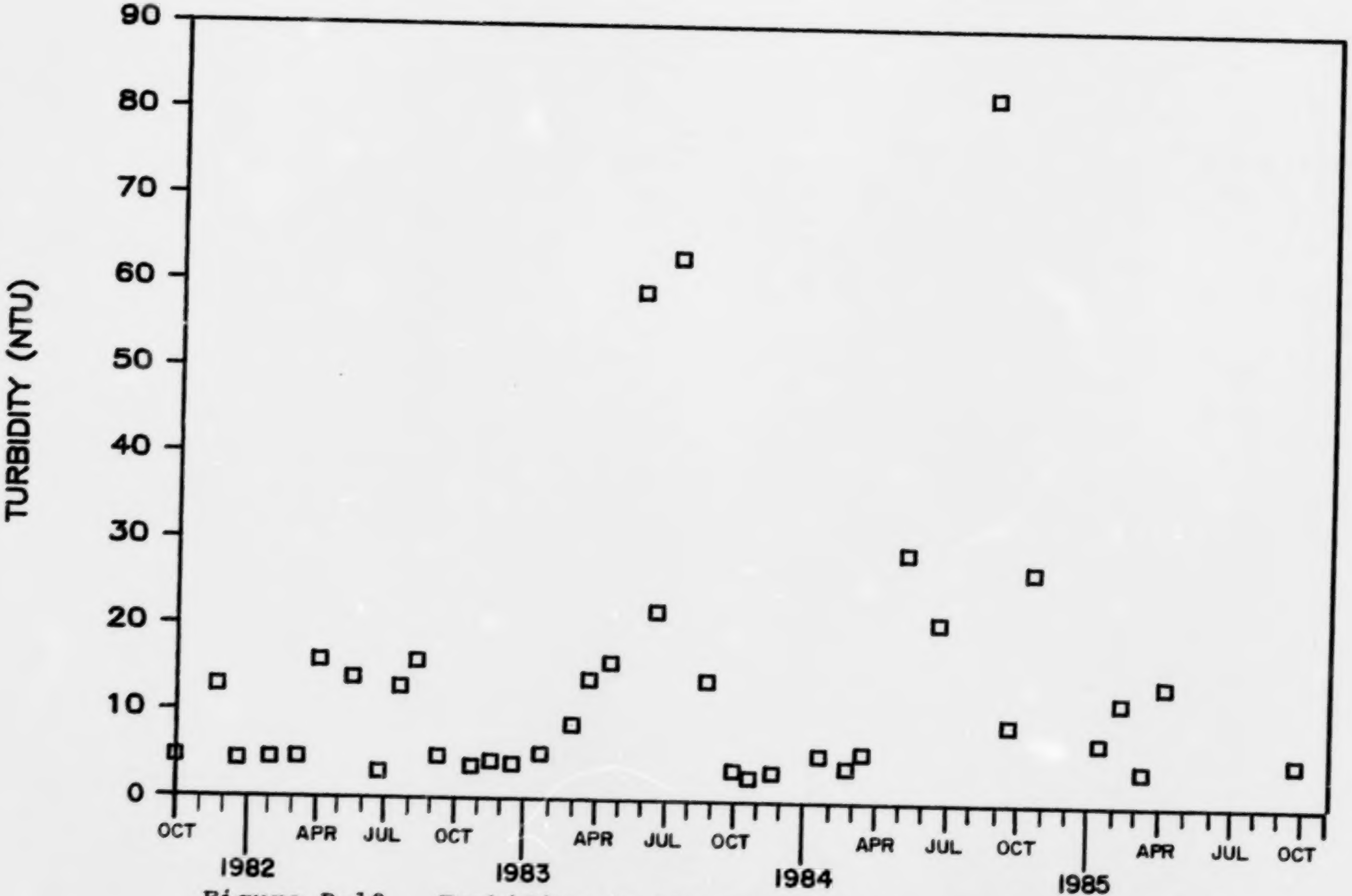


Figure B-18. Turbidity in the South Platte River upstream of the Metro discharge.

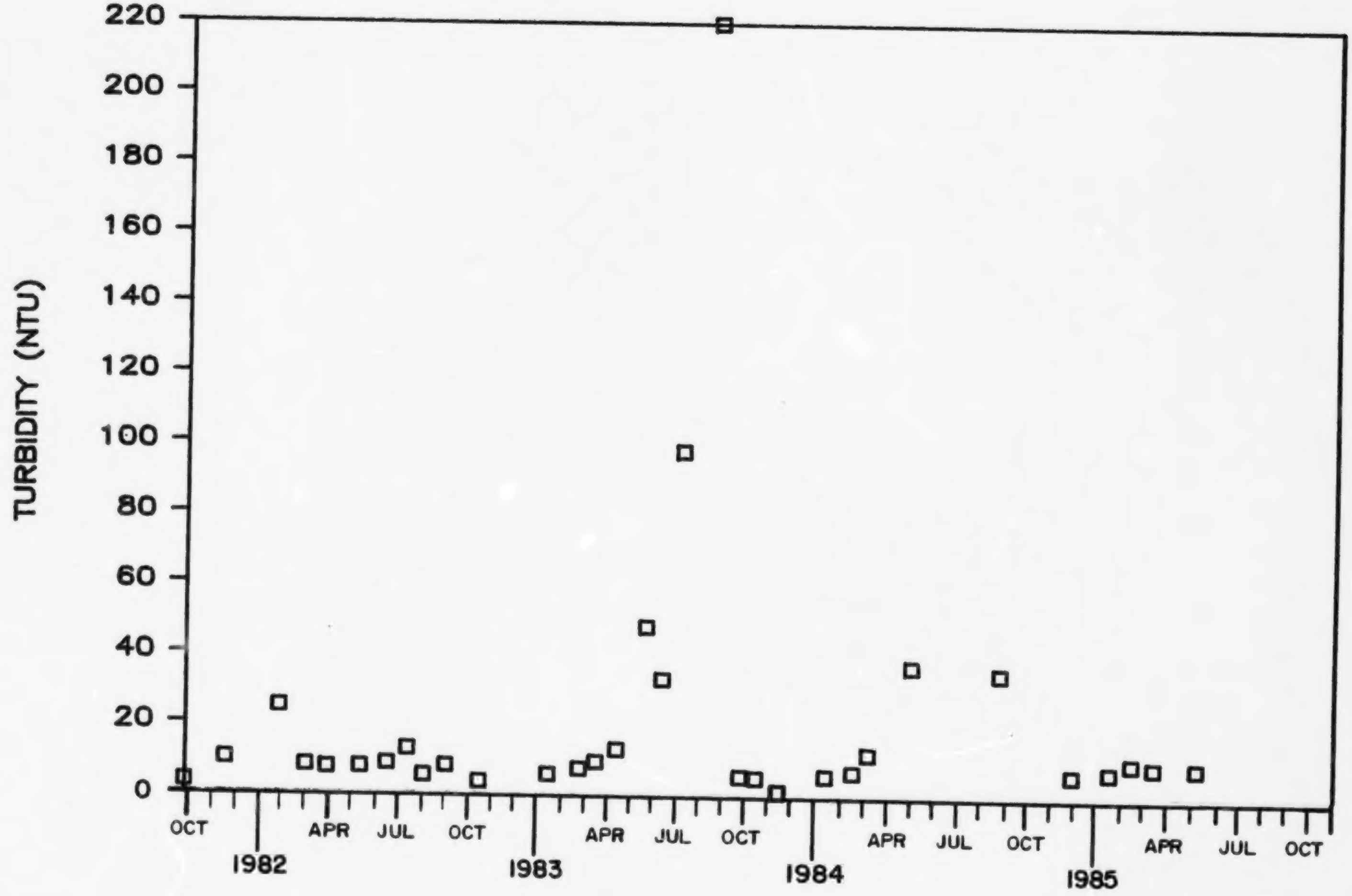


Figure B-19. Turbidity in the Lower Clear Creek ditch.

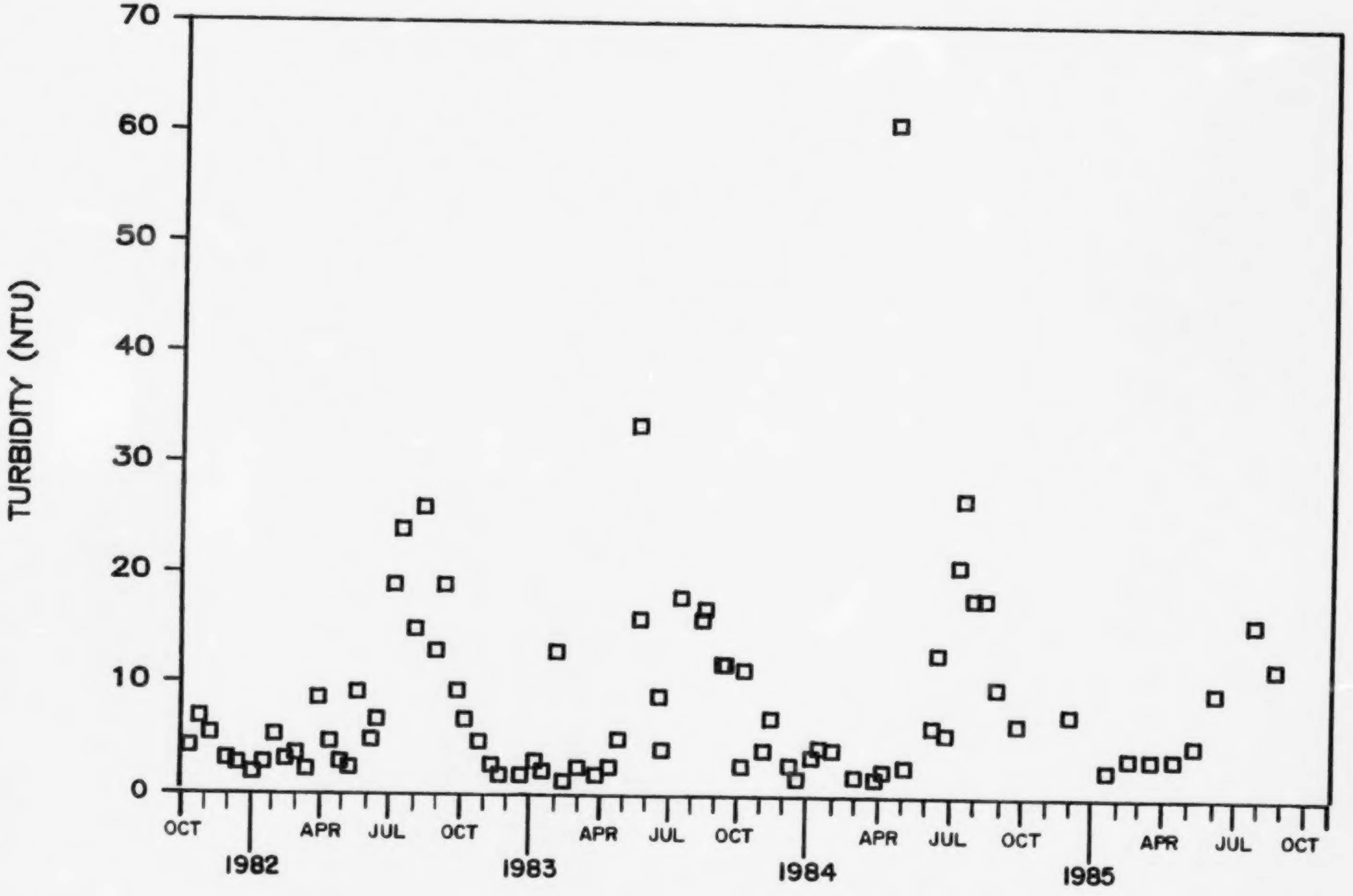


Figure B-20. Turbidity in the Standley Lake outflow.

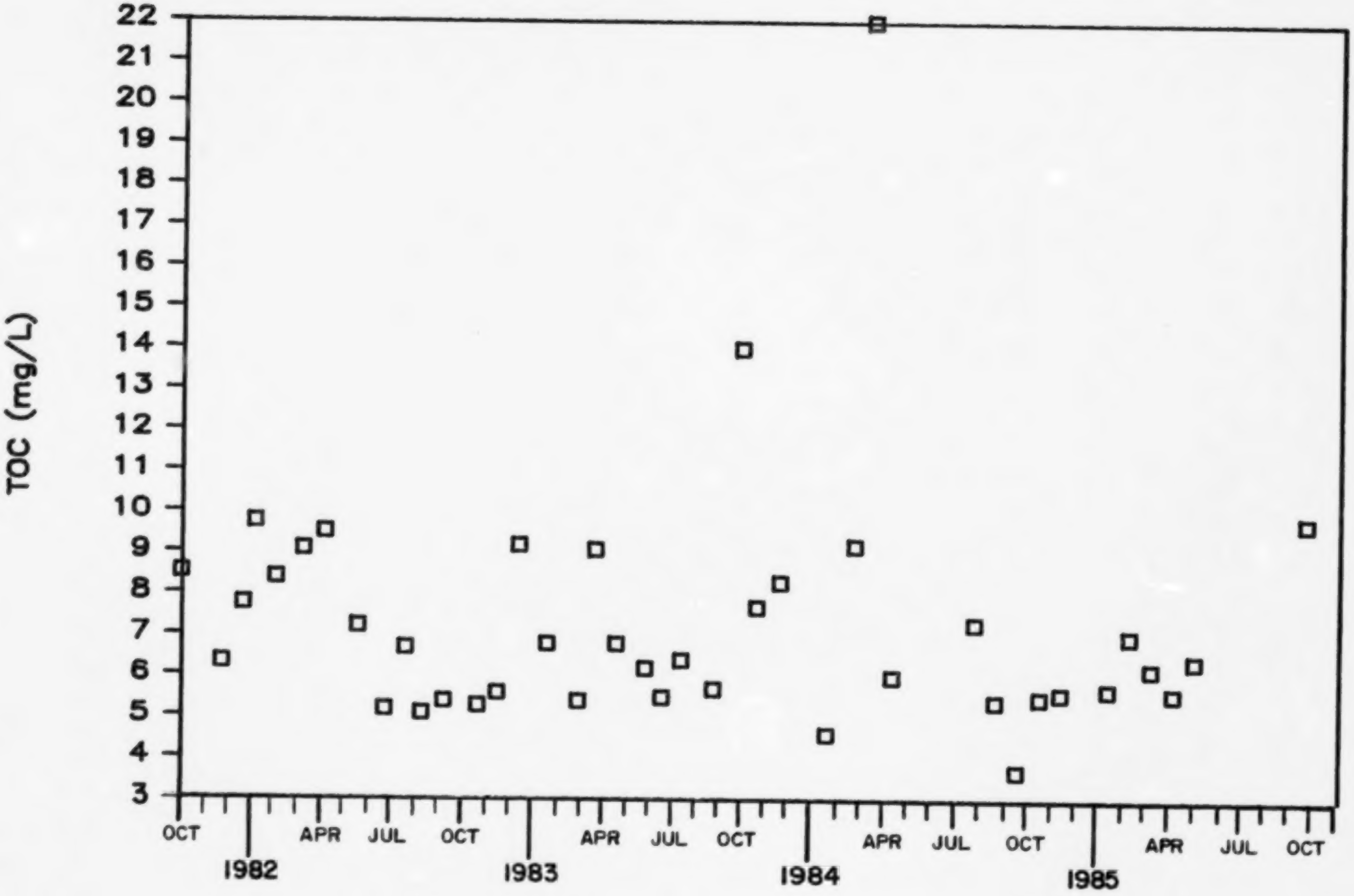


Figure B-21. TOC concentration in the Gravel Lakes.

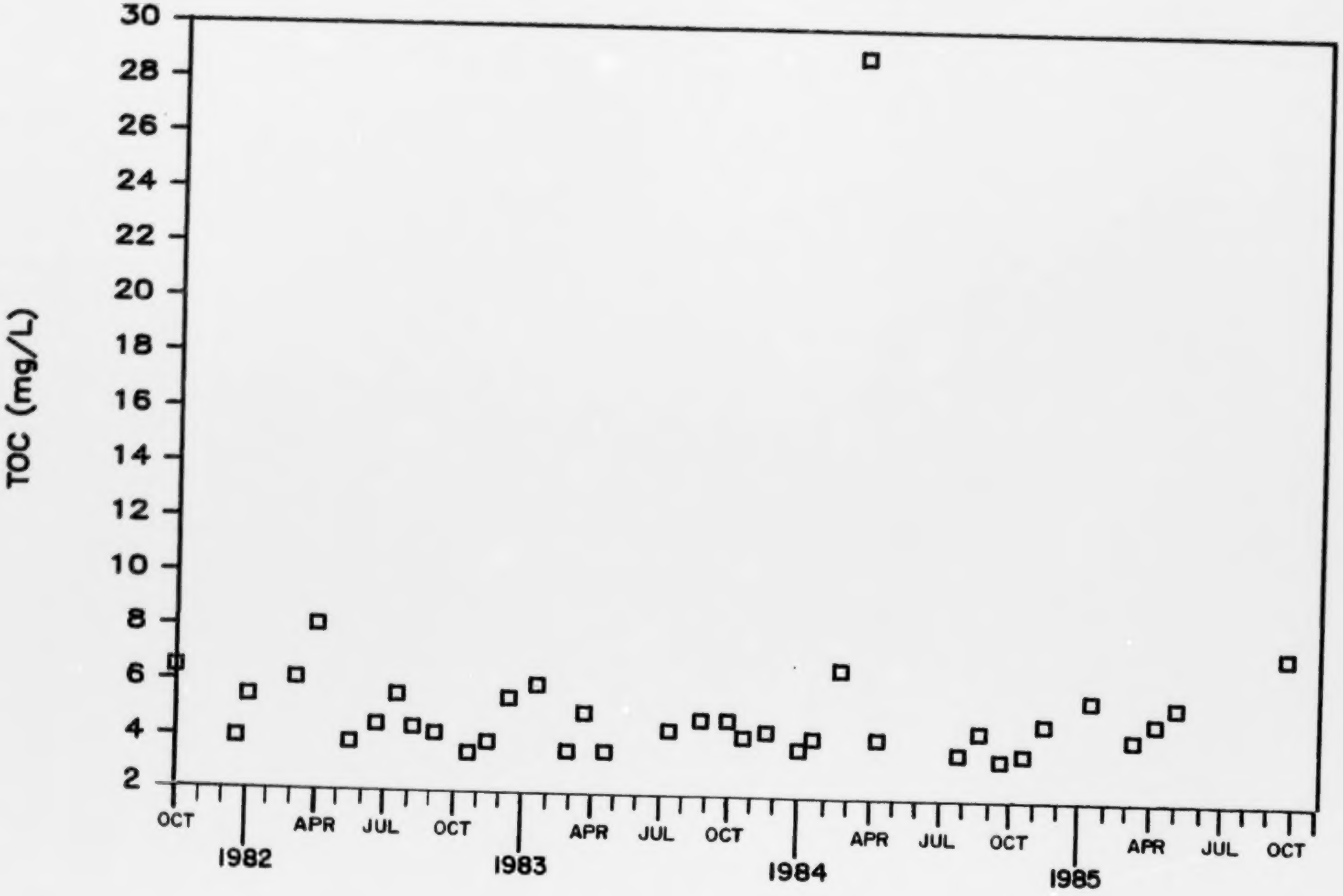


Figure B-22. TOC concentration in the Well Field.

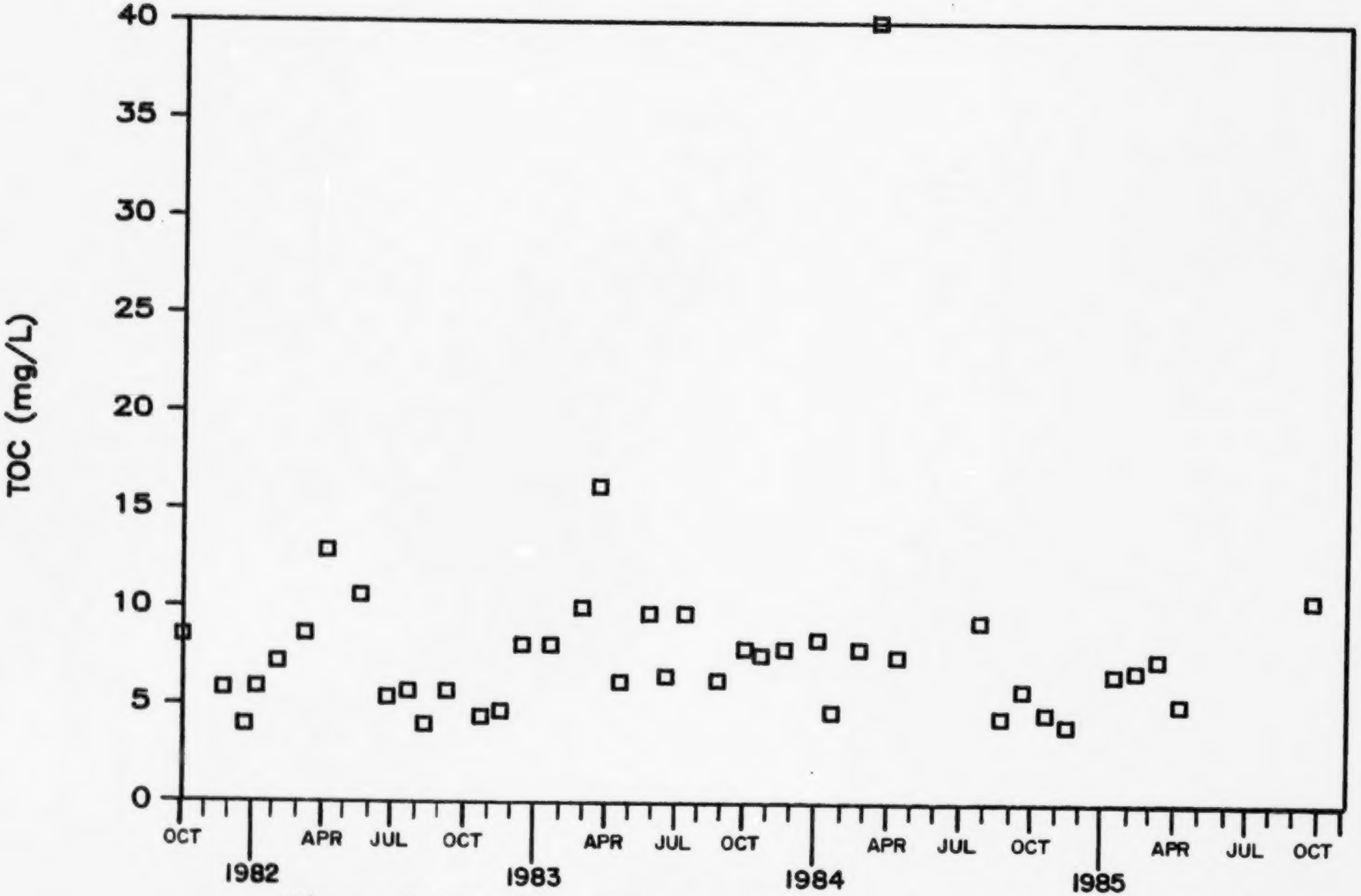


Figure B-23. TOC concentration in the South Platte River upstream of the Metro discharge.

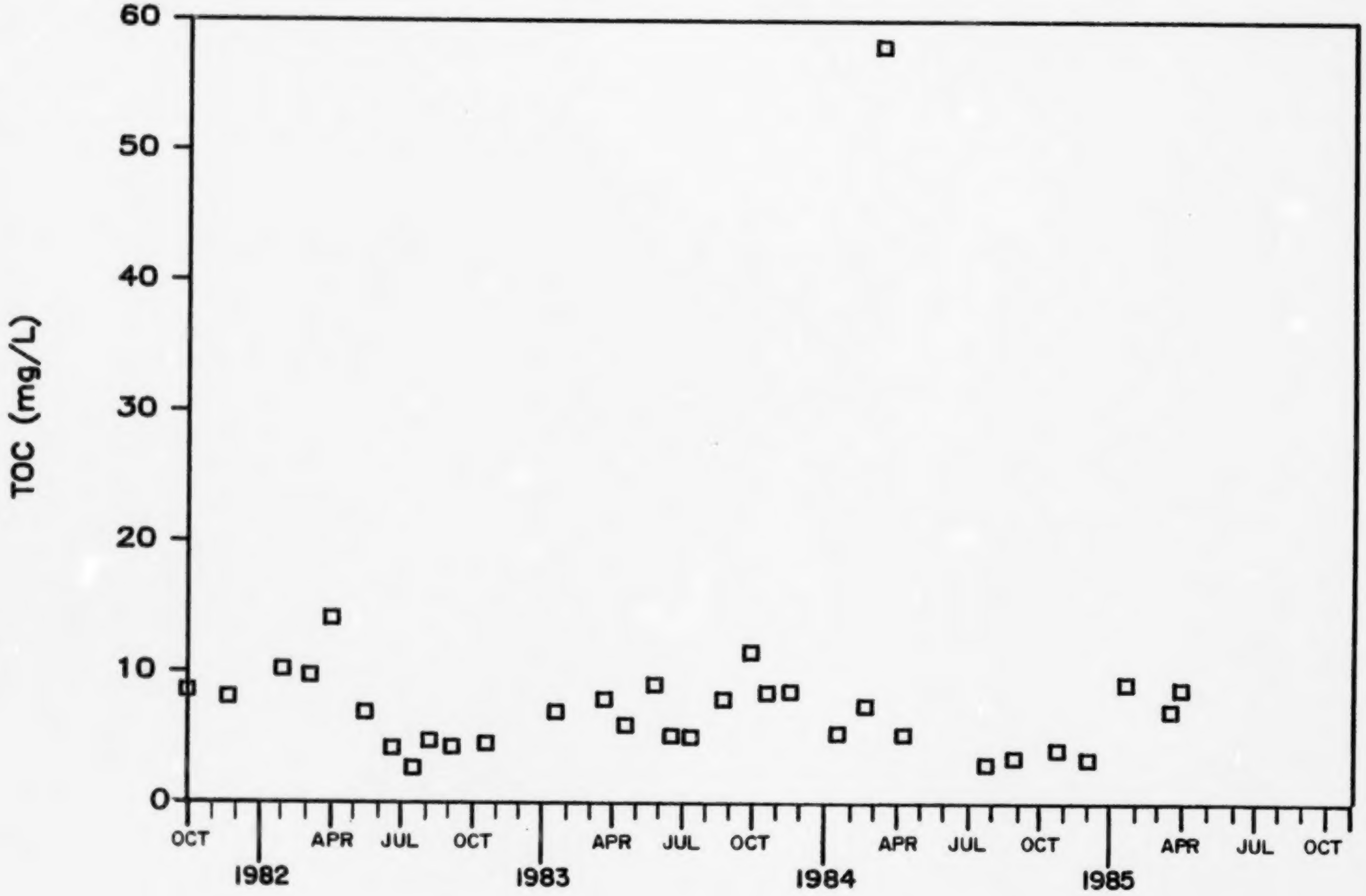


Figure B-24. TOC concentration in the Lower Clear Creek ditch.

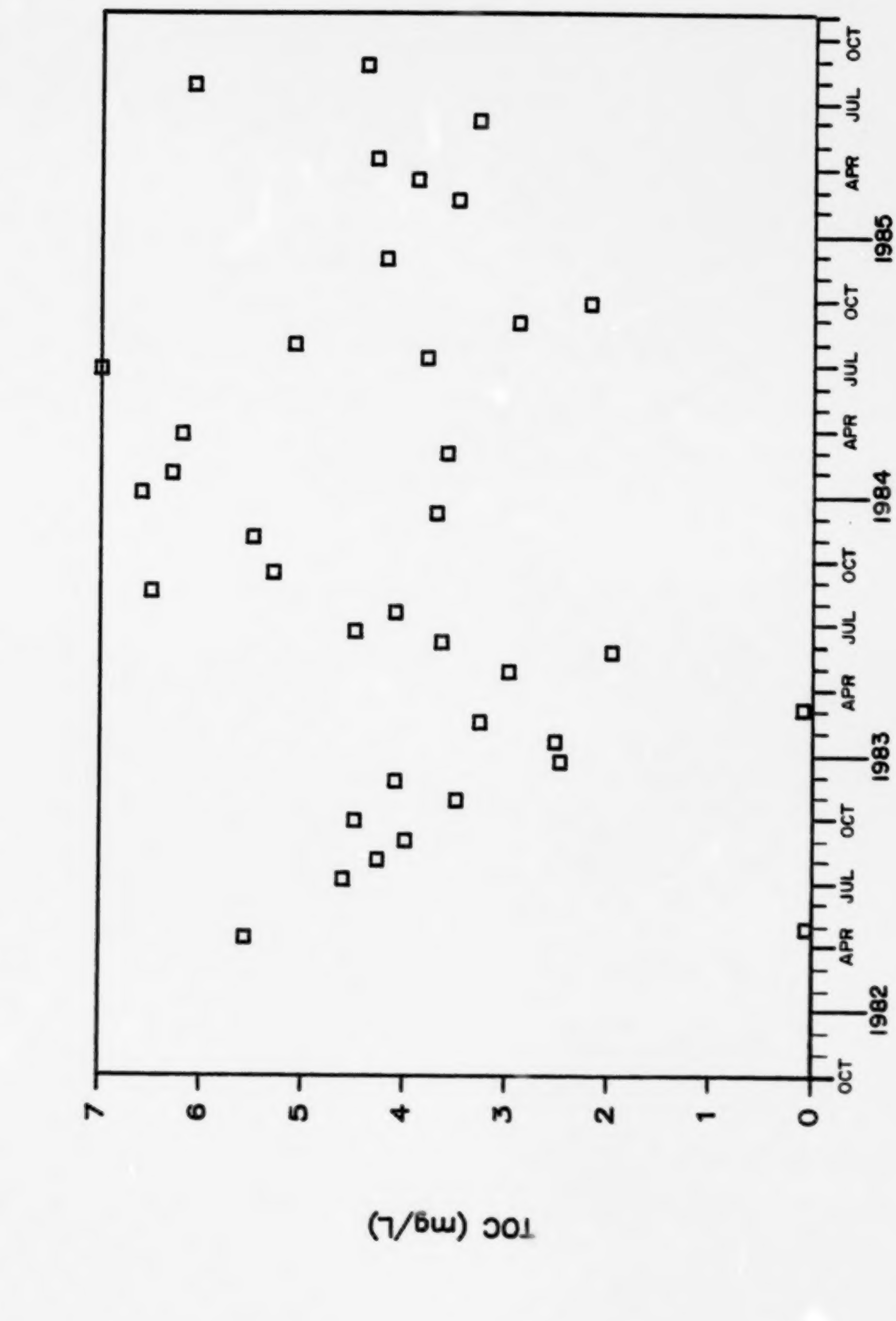


Figure B-25. TOC concentration in the Standley Lake outflow.

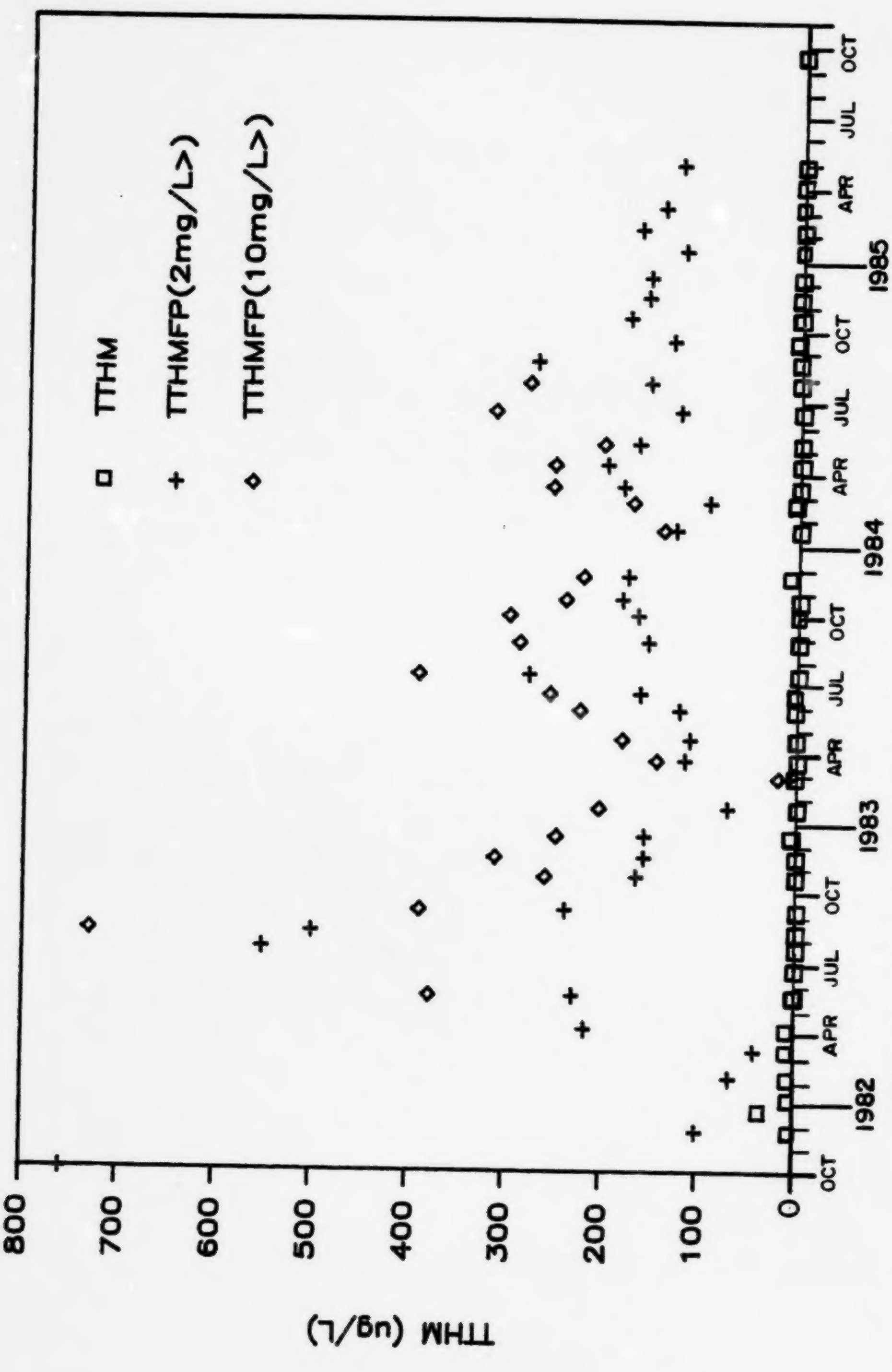


Figure B-26. TTHM and TTHMFP concentrations in the Gravel Lakes.

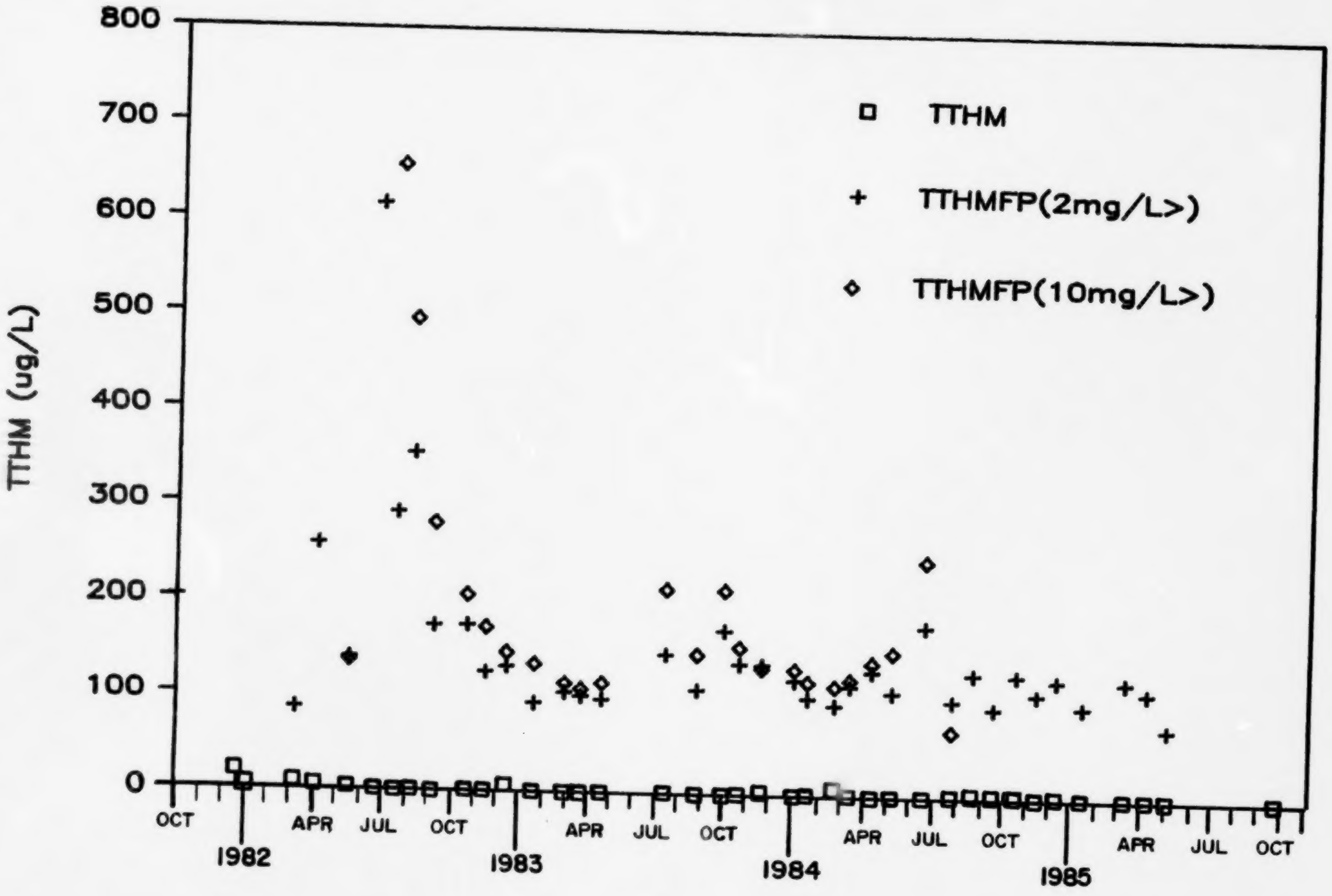


Figure B-27. TTHM and TTHMFP concentrations in the Well Field.

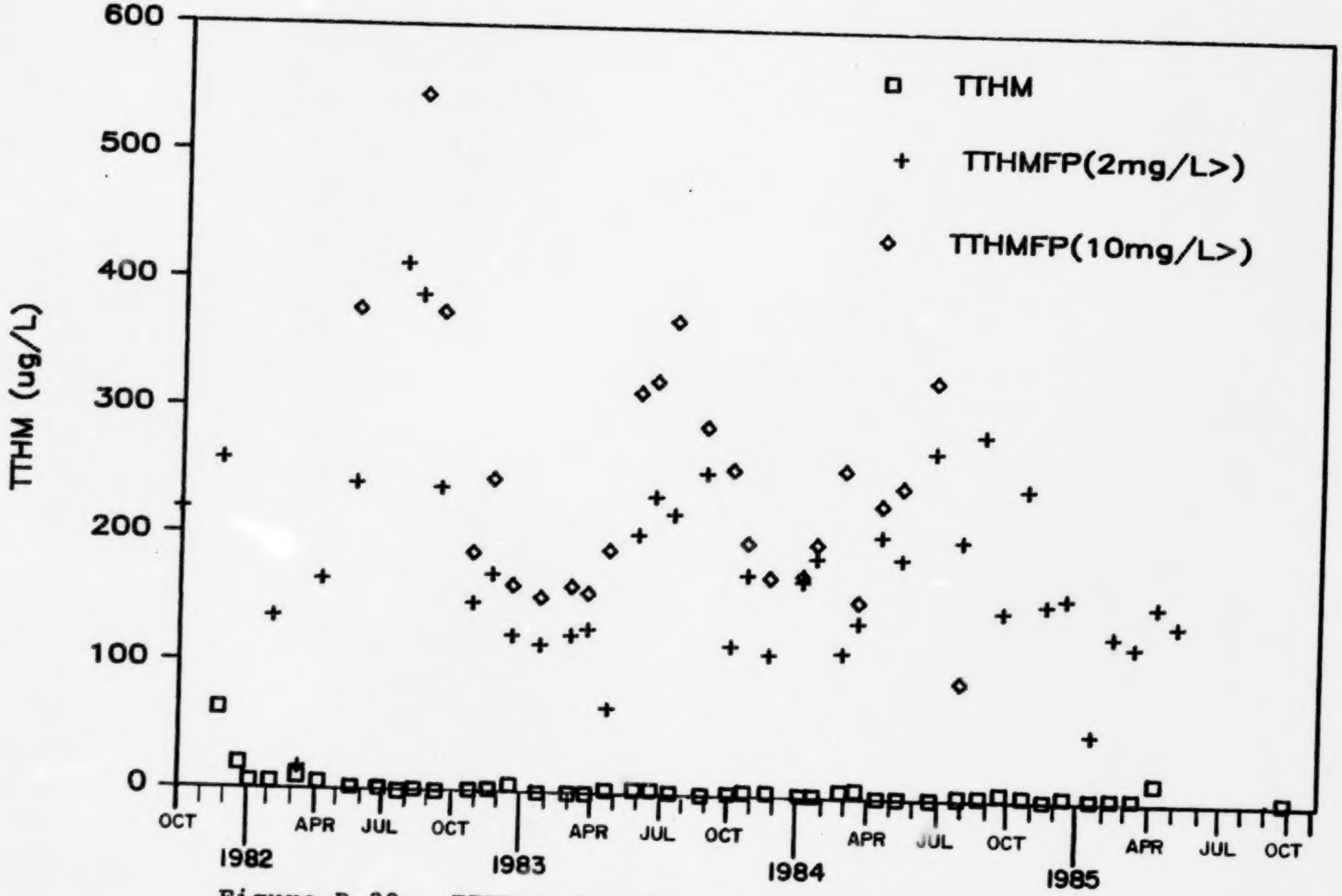


Figure B-28. TTHM and TTHMFP concentrations in the South Platte River upstream from the Metro discharge.

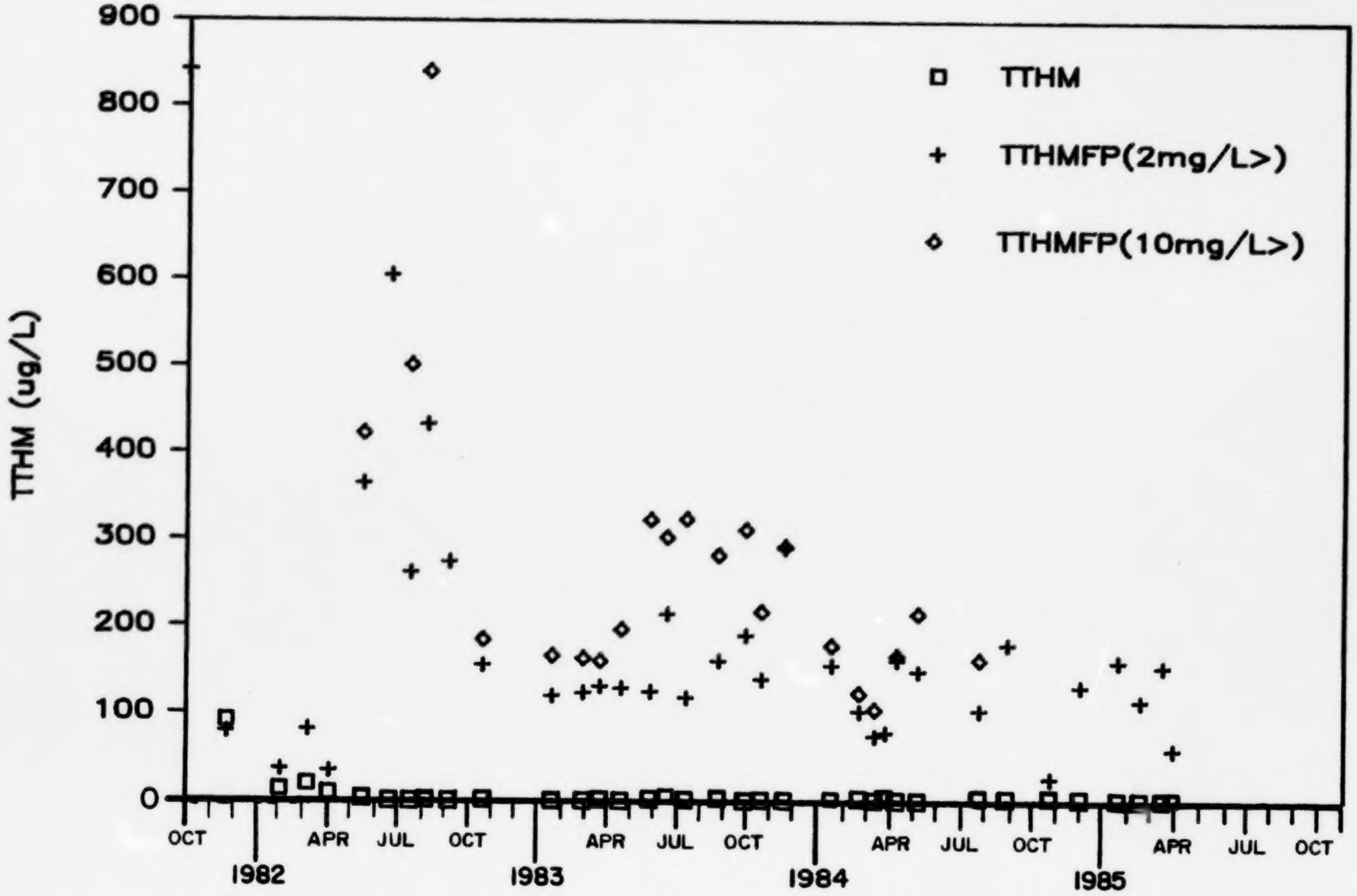


Figure B-29. TTHM and TTHMFP concentrations in the Lower Clear Creek ditch.

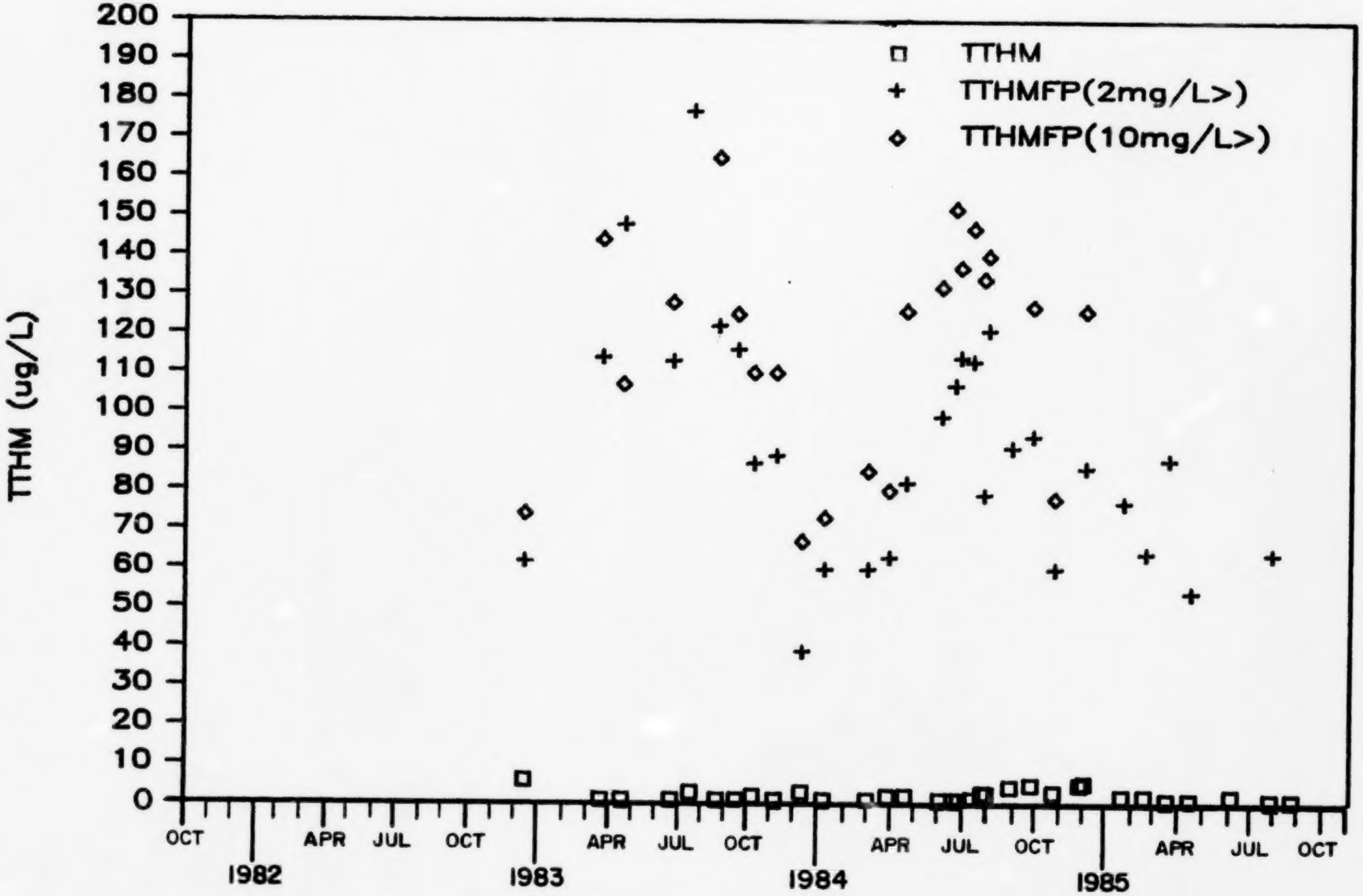


Figure B-30. TTHM and TTHMFP concentrations in the Standley Lake outflow.

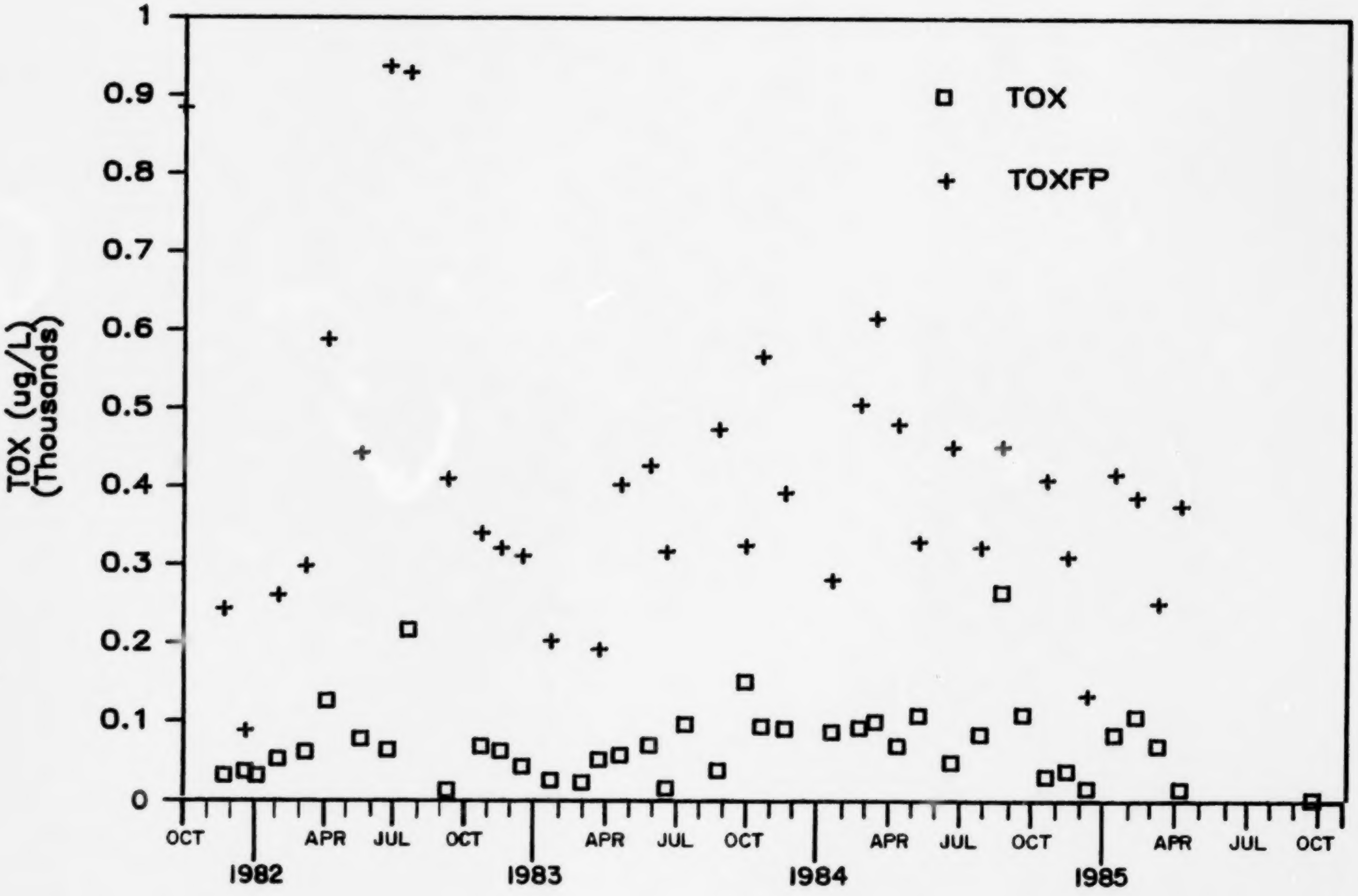


Figure B-31. TOX concentration in the Gravel Lakes.

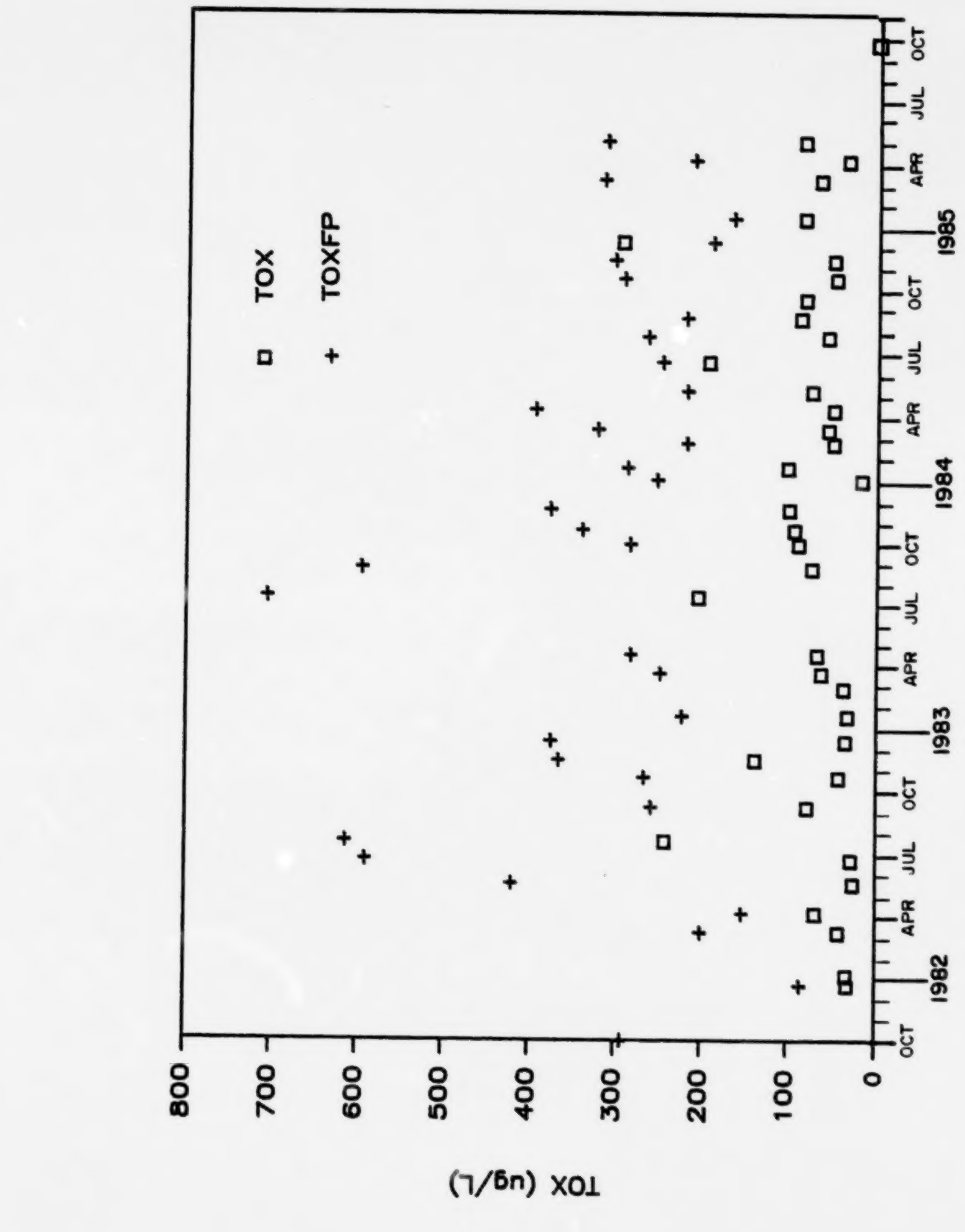


Figure B-32. TOX concentration in the Well Field.

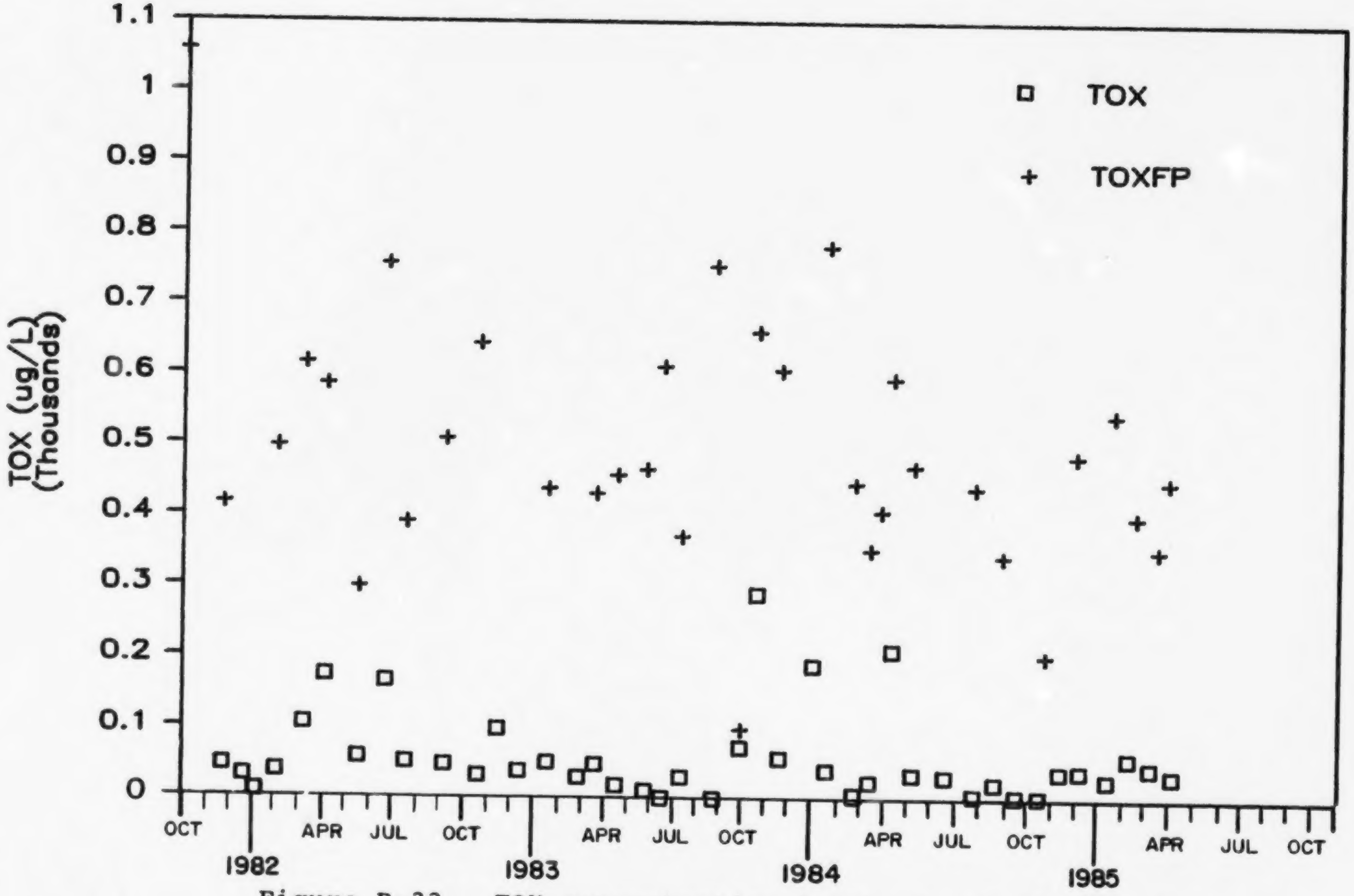


Figure B-33. TOX concentration in the South Platte River upstream from the Metro discharge.

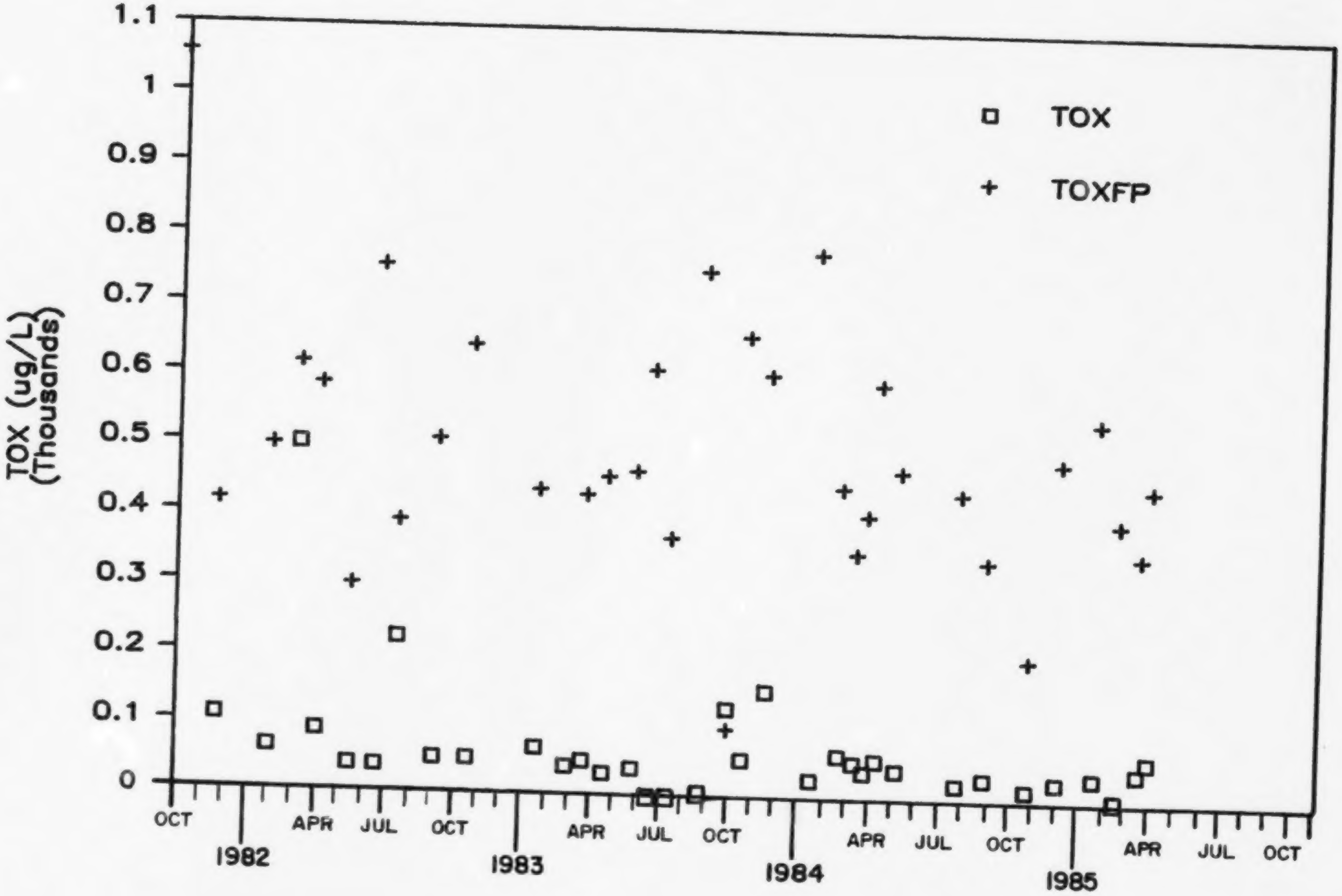


Figure B-34. TOX concentration in the Lower Clear Creek ditch.

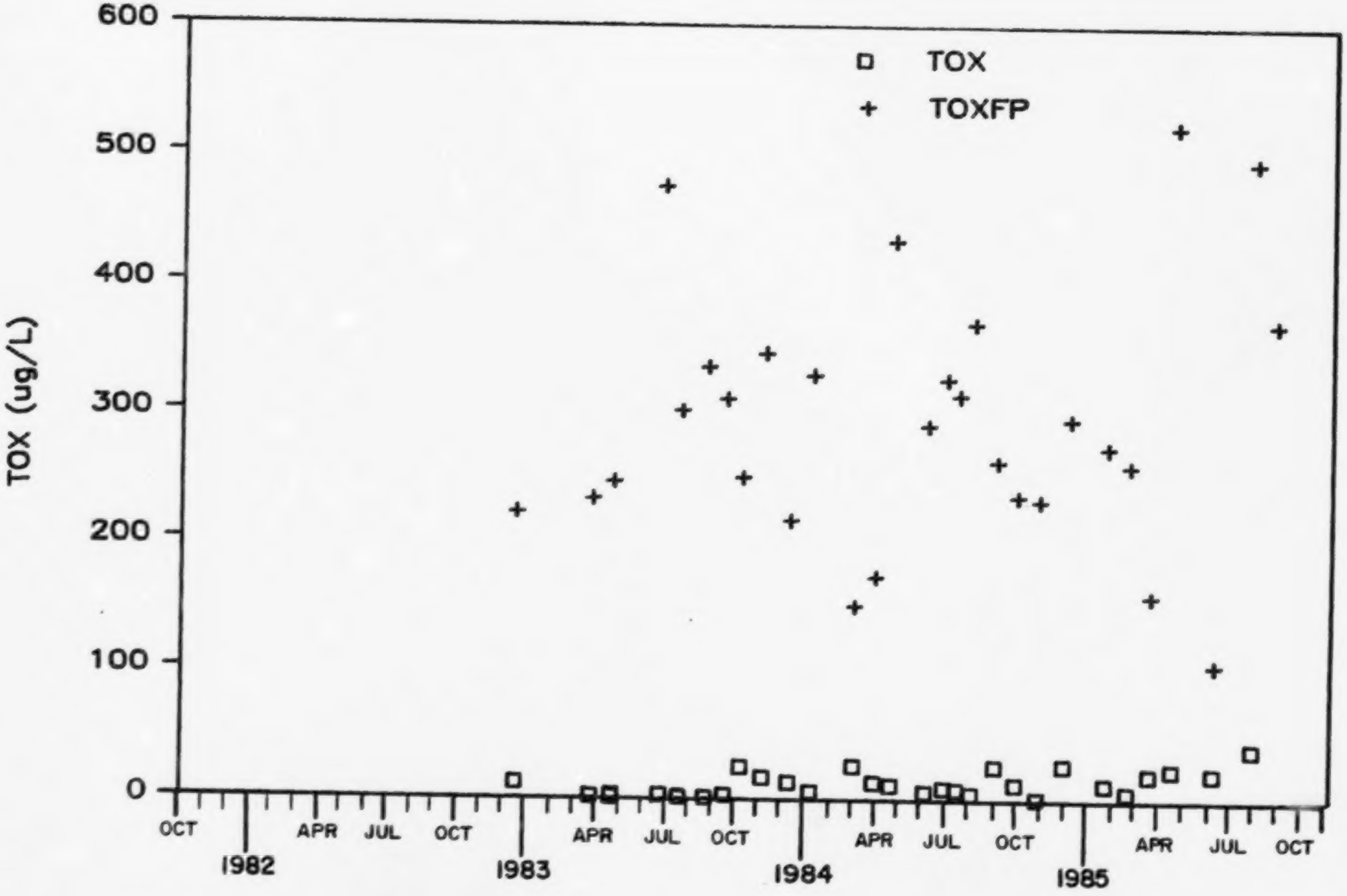


Figure B-35. TOX concentration in the Standley Lake outflow.

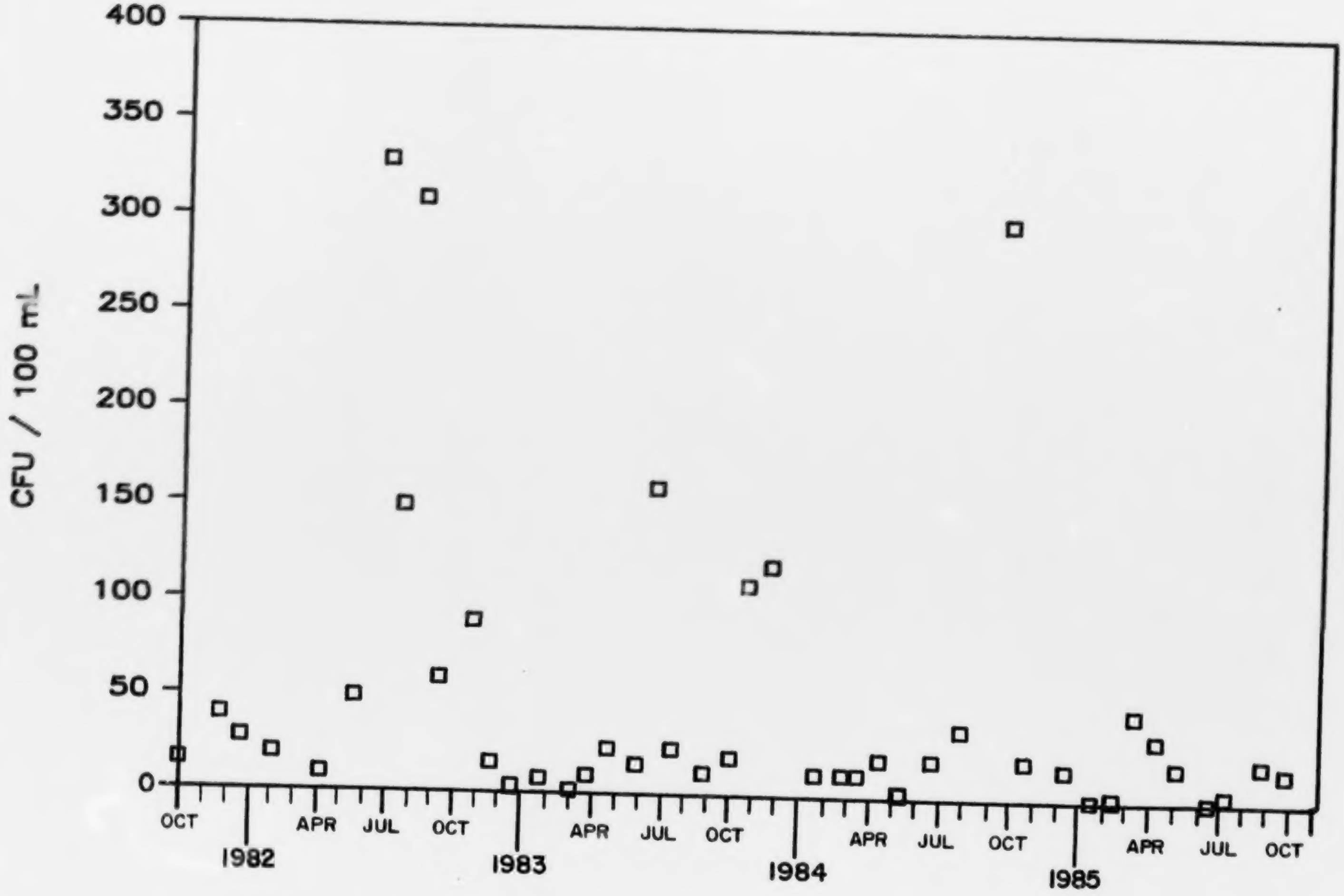


Figure B-36. Total coliform counts in the Gravel Lakes.

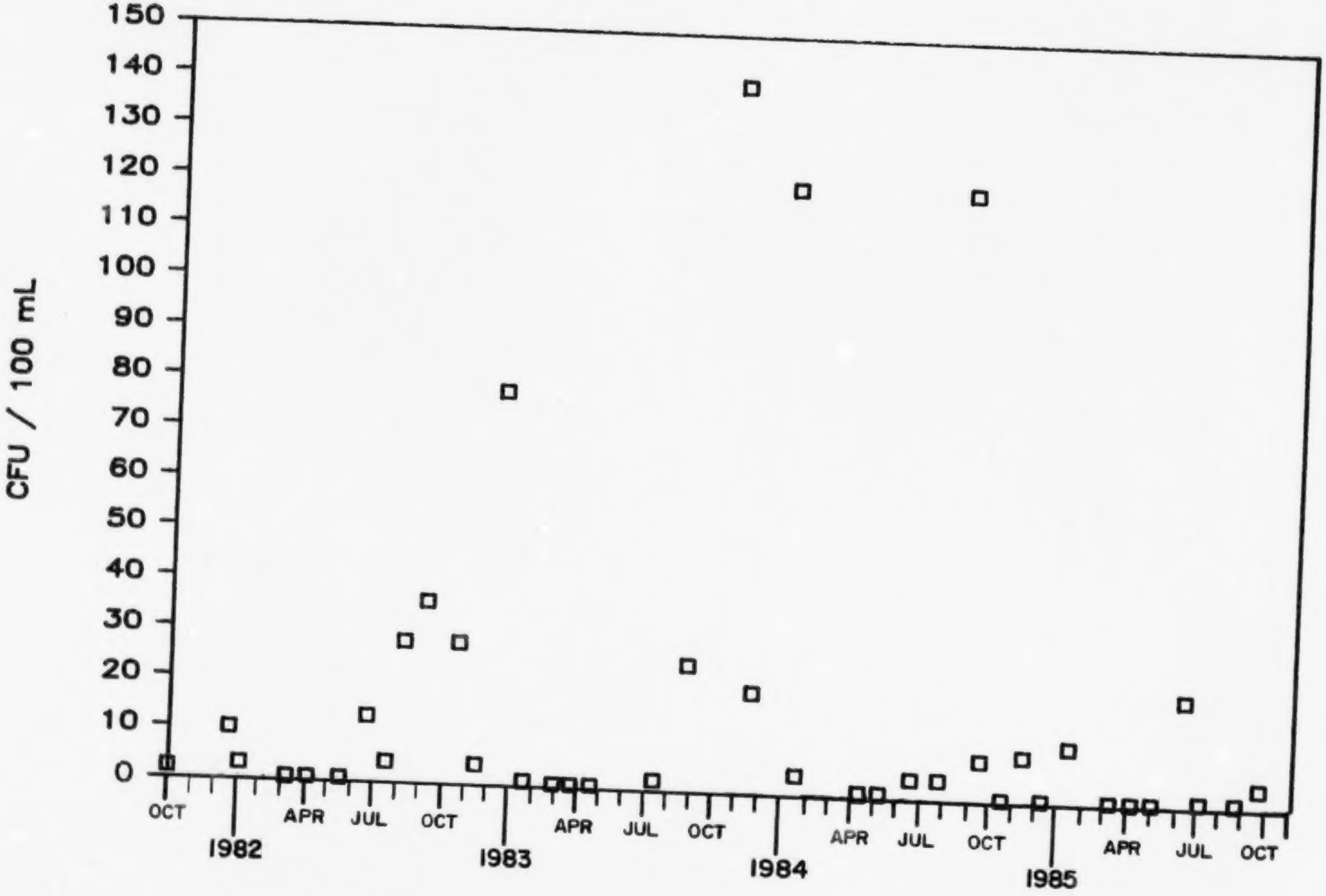


Figure B-37. Total coliform counts in the Well Field.

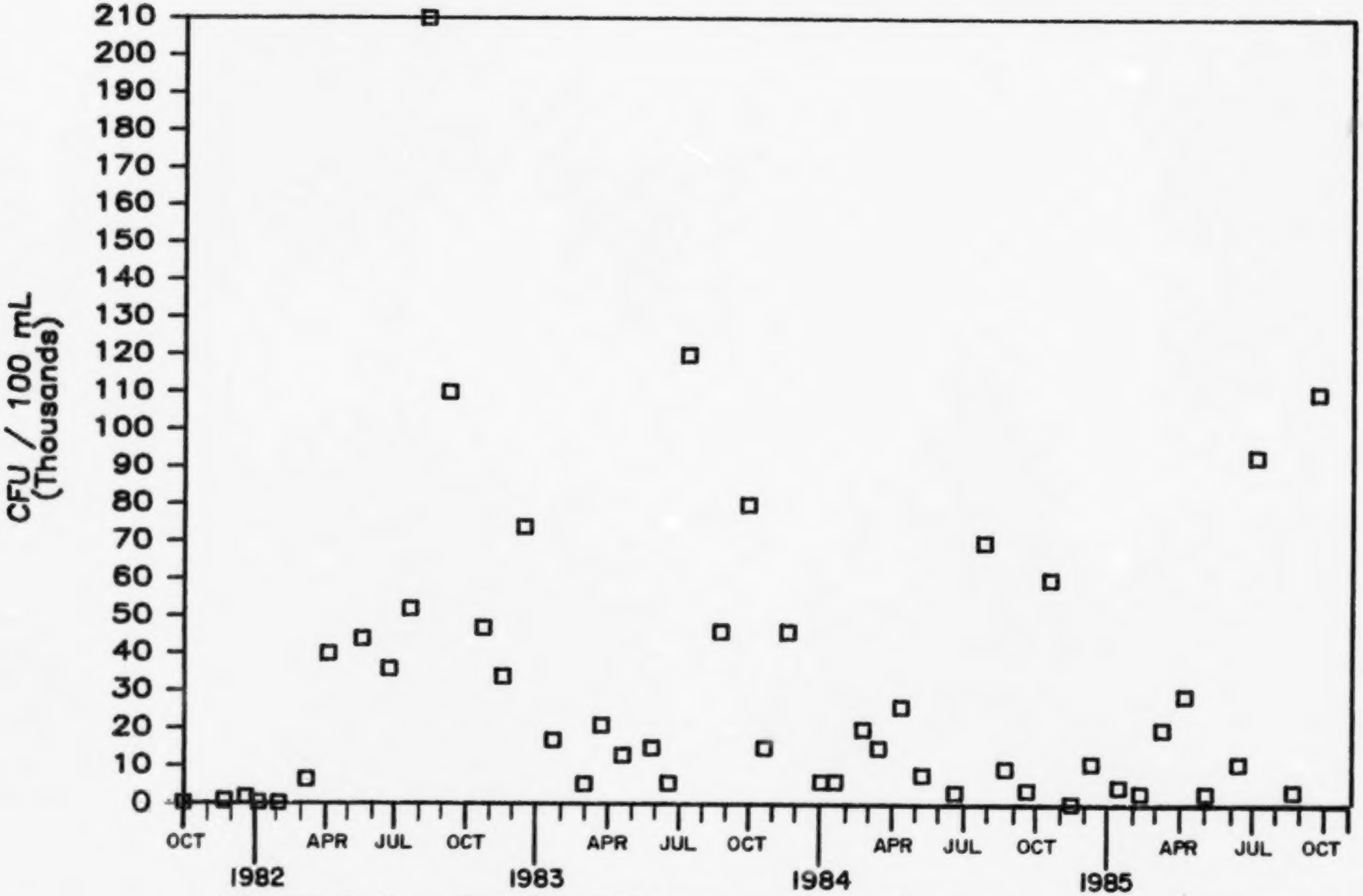


Figure B-38. Total coliform counts in the South Platte River upstream from the Metro discharge.

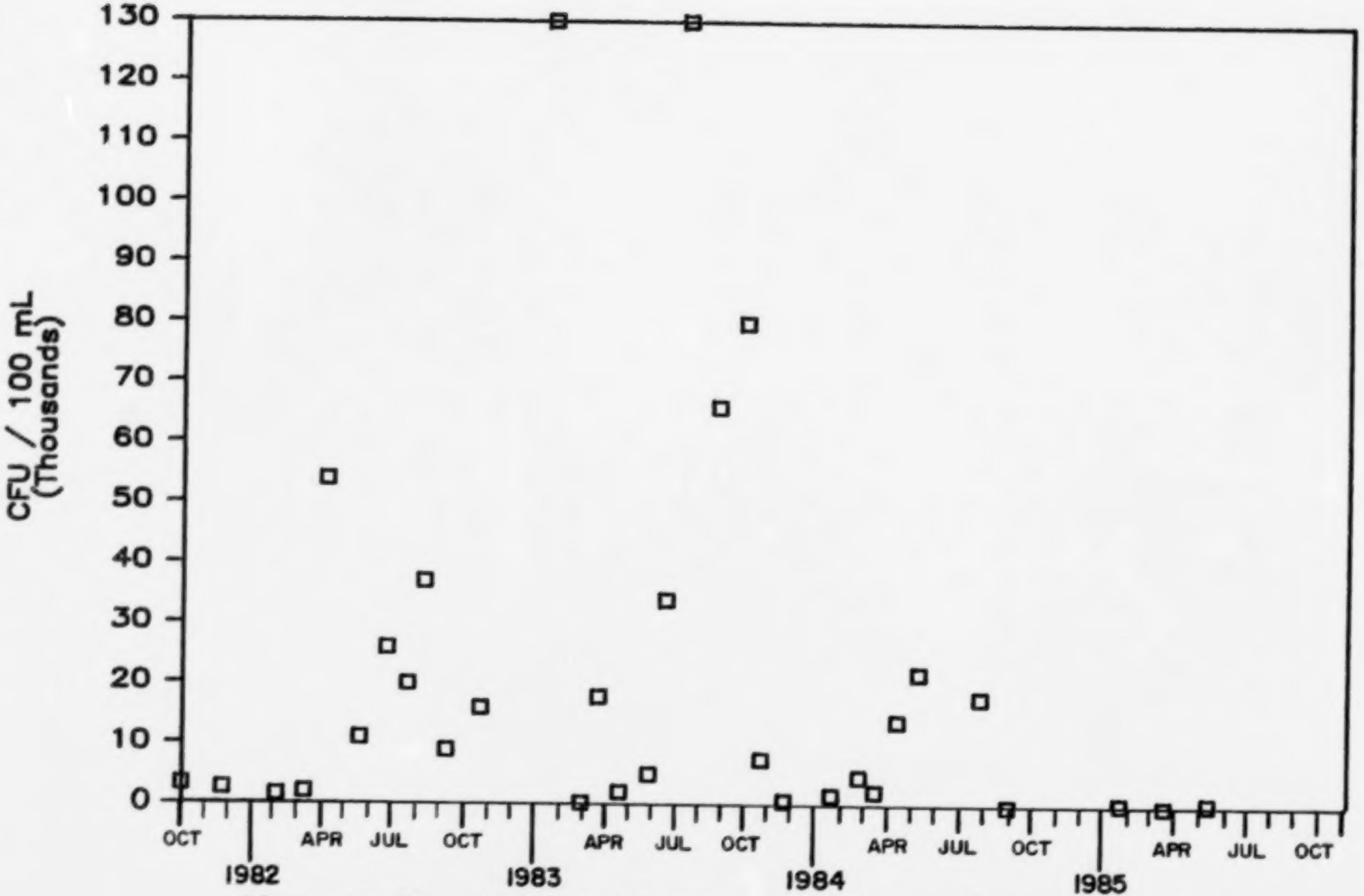


Figure B-39. Total coliform counts in the Lower Clear Creek ditch.

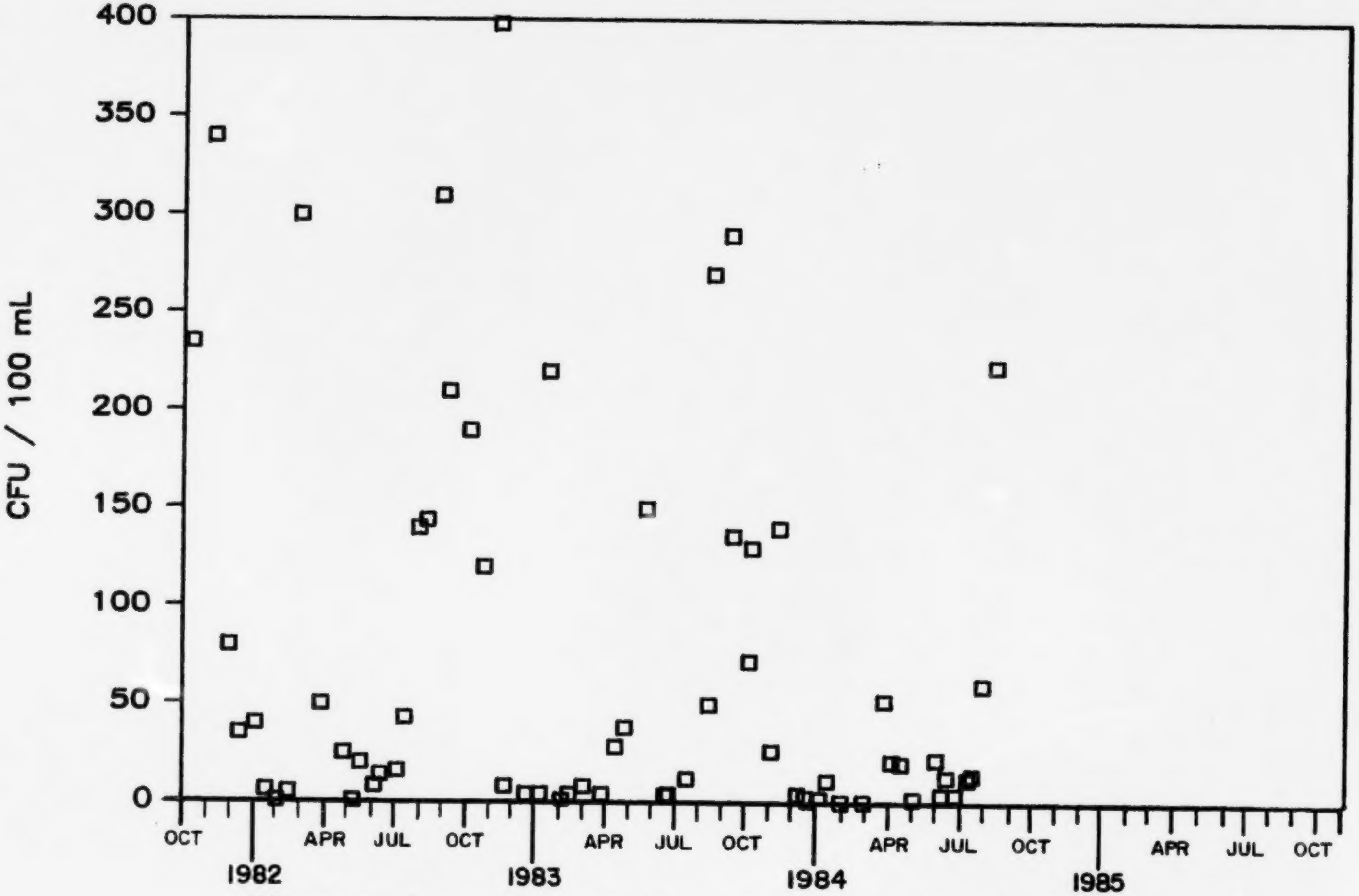


Figure B-40. Fecal coliform counts in the Standley Lake outflow.

APPENDIX C

FINAL REPORT - SIGNIFICANCE OF ORGANIC AMINO NITROGEN COMPOUNDS IN RAW WATER FROM THORNTON, COLORADO

During the course of the pilot plant program, special studies were conducted on specific areas of concern. A special study was conducted by Old Dominion University on the formation of trihalomethanes from the chlorination of organic amino nitrogen compounds. The final report of that project follows.

FINAL REPORT

SIGNIFICANCE OF ORGANIC AMINO NITROGEN COMPOUNDS IN RAW WATER FROM THORNTON, COLORADO

Dr. Frank E. Scully, Jr.
Principal Investigator
Department of Chemical Sciences
Old Dominion University
Norfolk, Virginia 23508

INTRODUCTION

Organic nitrogen compounds are abundant and essential components of nature. In several studies of natural waters[1,2] it has been found that dissolved organic nitrogen compounds comprise as much as a third of the total dissolved organic material. Organic nitrogen levels in natural waters can vary widely with water source and season, but levels of 0.5 to 1.0 milligrams per liter are not uncommon.[2-6] For instance, Speed has followed the yearly fluctuations of organic nitrogen concentrations in shallow gravel lakes which serve as the main drinking water supply for Thornton, Colorado. Levels in June have measured 3.8 mg/L, while in February levels of 1.2 mg/L are more typical.[3] Ram and Morris have found one freshwater source with as much as 21.7 mg/L organic nitrogen and correlated this with the bloom of a blue-green algae.[5] Several studies have attempted to subdivide the organic nitrogen fraction into amino nitrogen compounds and non-amino nitrogen compounds. Gardner[7] found that 20% of the dissolved organic nitrogen in a marine water sample was amino nitrogen, whereas in a freshwater system Gocke found as much as a third was organic amino nitrogen compounds.[1] All studies agree that the major portion of the amino nitrogen present in natural waters is tied up in proteins and polypeptides rather than as free amino acids.

The presence of high concentrations of proteins and amino acids in natural waters seems to be related to algal activity. For instance, Gardner and Lee[8] have found substantially higher concentrations of amino acids during a period of rapid algal decomposition. Tuschall and Brezonik[2] have found that 71% of the dissolved organic nitrogen in the filtrate of a culture of Anabaena sp. was proteinaceous. The full implications of these observations for the treatment of natural water affected by algae growth have not yet been fully realized, but Williams[9] has described problems of taste, odor, disinfection requirements, and cost of treatment associated with the presence of proteins in drinking water supplies.

Oliver *et al.*[10] and Hoehn *et al.*[11,12] have recently reported that algae, both their biomass and their extracellular products, can be important sources of trihalomethane precursors. Because amino acids and proteins are important intercellular components of all cells as well as extracellular by-products of algae cultures, algae growth and seasonal variations of trihalomethane production from chlorination seems to be related to the presence of proteinaceous nitrogen compounds in some natural waters. The question of whether this relationship is direct or coincidental has been part of the rationale for the study described here.

Since Morris *et al.*[13] have demonstrated that several of the basic amino acids which are found in nature can produce chloroform in chlorinated water, a study was undertaken to evaluate the significance of proteins in the production of trihalomethanes in both natural and model water systems and to assess the effectiveness of current treatment methods for their removal.

The main source of raw water for the City of Thornton, Colorado is a series of shallow gravel lakes which are adjacent to the S. Platte River one mile downstream from the discharge point of the Denver Metro Wastewater Treatment Plant. Besides periodic groundwater intrusion from the river, the lakes are affected regularly by algae blooms. Throughout the year they are found to be hign in ammonia and dissolved organic nitrogen. Therefore, one objective of this project was to characterize chlorinated by-products of water treatment other than the trihalomethanes, specifically organic N-chloramines.

EXPERIMENTAL

General

Model proteins used in this work were obtained from Sigma Chemical Co. To determine the yield of chloroform from chlorination of proteins stock solutions of the proteins were prepared in chlorine demand free water and dialyzed overnight against deionized water using dialysis tubing with a molecular weight cut-off of 8,000 (A.H. Thomas). These dialyzed stock solutions were quantitated spectrophotometrically before they were diluted to the desired concentration with chlorine demand free water. Control experiments showed that in all but one case (rennin) dialysis did not reduce the amount of chloroform produced.

Trihalomethane Analysis

Solutions were chlorinated with standard hypochlorite (1000 ± 10 mg/L) prepared as described in EPA Method 510.1. Trihalomethanes were isolated and analyzed by the liquid/liquid extraction method prescribed by EPA protocol.[14]

Protein Analysis

Samples of raw water were obtained in one liter glass bottles and sealed without headspace using Teflon-lined caps. The samples were shipped overnight to Norfolk where they were refrigerated at 4 °C. They were analyzed within one week for protein concentration. Dissolved hydrolyzable amino acid nitrogen levels (protein concentrations) were measured by a variation of the method of Gardner and Stephens.[7] To eight vacuum hydrolysis tubes were added 0.5 mL aliquots of a sample of water to be analyzed. Standard additions of glycine were made to the tubes followed by 0.5 mL of a 50% solution of distilled propionic acid and ultrapure concentrated HCl.[15] The samples were hydrolyzed for 30 min. at 145 °C, cooled, and lyophilized before being derivatized with fluorescamine and analyzed for fluorescence emission at 480 nm (excitation at 390 nm).

Preparation of Raw Water Samples for Amino Acid and Chloramine Analyses

A sample of water taken on 9/11/1985 was filtered upon receipt through a 0.35 µm glass fiber filter, frozen, and stored at -80 °C in a freezer. A 2000 mL sample of the filtrate was thawed and its pH adjusted to 2.5 with ultra-high purity concentrated hydrochloric acid. It was then placed in a clean round-bottomed flask, and concentrated to dryness by freeze-drying. The residue was dissolved in 20 mL of the original filtered lake water (pH approximately 7-7.5). Not all of the solid residue dissolved, so the concentrate was filtered through a 0.35 µm glass fiber filter. This concentrate was used in the analysis of amino acids and organic N-chloramines formed in Gravel Lake water.

Analysis of Amino Acids in Gravel Lakes

A portion of the concentrate was passed through a 0.45 μm teflon filter and 70 μL was analyzed by HPLC using the Waters AUTO*TAG automatic pre-column derivatization technique. This method involved automatic derivatization of the amino acids with ortho-phthalaldehyde (OPA), chromatography on a Waters Assoc. RESOLVE 5 μm C_{18} stainless steel chromatography column, and fluorescence detection. The OPA derivatizing solution was prepared by dissolving 250 mg OPA in 5 mL methanol and diluted to 50 mL with a saturated aqueous solution of sodium tetraborate decanydrate ($Na_2B_4O_7 * 10\ H_2O$). The Waters model 710B autosampler (WISP) and solvent programmer were programmed in the following manner:

Time	% Solvent A	% Solvent B	Flow Rate (mL/min.)	Curve No.
0	100	0	0	*
2	100	0	0.1	6
2.5	100	0	1.0	6
10	80	20	1.0	6
15	70	30	1.0	6
16	70	30	1.0	6
50	40	60	1.0	6
55	40	60	1.0	6

A standard solution of amino acids (2.5×10^{-3} M in 0.1 N HCl)

Reproduced from best available copy.

was obtained from Sigma Chemical Co. and diluted 250-fold to 10 μM. This standard solution (10 μL) and a blank were analyzed in the same manner as the Gravel Lake concentrate in order to identify and quantitate the amino acids present.

Analysis of Organic N-Chloramines Formed on Chlorination of Gravel Lakes Water

Two 2 mL aliquots of the concentrate described above were chlorinated to 300 ppm and 500 ppm Cl_2 (100 times the original chloramine maximum), incubated at room temperature in the dark for 24 hours, and derivatized with dansyl sulfinic acid overnight in an equal volume of acetonitrile as described previously. The derivatized sample was concentrated to remove the acetonitrile, the pH adjusted to 3 with concentrated phosphoric acid, and passed through a pre-conditioned Waters Assoc. C_{18} SEP-PAK. The SEP-PAK was eluted with 1 mL acetonitrile. A 400 μL sample of the eluate was analyzed by HPLC on a 30 cm Alltech stainless steel column packed with 10 μM octadecylsilane. The solvents used to elute the dansyl derivatives included 0.1 M potassium acetate adjusted to pH 4.4 with conc. formic acid (Solvent A) and a mixture of 45% Solvent A, 40% acetonitrile, and 15% 2-propanol (Solvent B). A flow rate of 1.5 mL/min. was used throughout the chromatogram. The elution pattern included a 6 min. initial isocratic elution with 20% Solvent B/80% Solvent A, followed by a linear gradient from 20% B to 80% B over the next 40 minutes. This was followed by an isocratic elution at 80% B for six minutes before the final linear gradient from 80% B to 100% B over 15 min. A reagent blank was chlorinated and derivatized in the same manner as the sample of the concentrate. Standard dansyl amino acids were chromatographed under identical conditions.

RESULTS AND DISCUSSION

Yields of THMs from Proteins

Four commercially available proteins were chosen as models of proteins present in nature. They were chosen for their different molecular weights which span the range found by Tuschall and Brezonik.[2] Bovine serum albumin (BSA) is a readily available compound frequently used in model studies because its purity, secondary and tertiary chemical structures, activity, and function have been well characterized by biochemists. It has the highest molecular weight of the compounds examined. Pepsin and rennin are digestive enzymes found in the stomachs of many mammals. Cytochrome c, which contains an iron-porphyrin group, is a pigmented protein used by aerobic cells to transfer electrons to oxygen. Although the structure of cytochrome c isolated from different cells varies slightly, a cytochrome of the c-type has been isolated from blue-green algae.[16]

Five-day terminal trihalomethane concentrations were measured using solutions of each protein with a carbon content of 2-3 mg/L in 0.025 M potassium phosphate at pH 7.0, chlorinated to 20 mg/L Cl_2, and incubated in the dark at 20 °C. The results are recorded in Table I. Humic acid obtained from Aldrich Chemical

Co. was used as a comparison. Surprisingly, the yields of chloroform produced by proteins of widely varying structure and molecular weight are quite similar. Although they seem low, they are about half that of humic acid which also gives low yields.

Modeling of Proteins vs Humic Acid

Since the yield of chloroform from BSA appeared to be representative of that of other proteins, BSA was chosen as a model for studying the production from proteins. Figure 1 is a plot of the chloroform produced with time when a solution of either BSA (5 mg/L) or humic acid (HA)(5 mg/L) is chlorinated to an initial concentration of 20 mg/L. Qualitatively, the curve obtained for the formation of chloroform from BSA is similar in shape to that obtained from the chlorination of humic acid. However, there is one noteworthy difference. The trihalomethane formation from BSA is much slower than that from humic acid at incubation times less than 24 hours. It is quite likely that before chloroform can be produced from the reactive sites on the protein, the protein must be oxidized sufficiently to allow the protein to unfold enough to expose these sites.

The effect of increasing the initial Cl_2 dosage on the chloroform produced from a constant concentration of protein over five days is plotted in Figure 2. Five milligrams of BSA contains 2.2 mg of TOC. Therefore, from Figure 2 it can be seen that up to a Cl_2/TOC weight ratio of one increasing the chlorine concentration has no significant effect on the chloroform production. Between a Cl_2/TOC ratio of one and five the chloroform production increases, but above a ratio of about five to one increasing the chlorine concentration has little effect. These results are very similar to those of Amy[17] who studied humic acid. However, one additional fact should be noted. On the same graph are plotted the total residual chlorine levels measured shortly before the solutions were analyzed for chloroform. It can be seen that there is no residual chlorine remaining after five days to produce more chloroform when solutions were chlorinated to a Cl_2/TOC ratio below five to one. This is presented in a slightly different fashion in Figure 3 which shows the effect of increasing the Cl_2/TOC ratio on the trihalomethane formation over a period of five days. It appears that doubling the chlorine concentration from 10 mg/L to 20 mg/L doubles the amount of chloroform produced. However, it should be pointed out again that there is no free residual chlorine remaining by 72 hours after initially dosing solutions to 15 mg/L or less. Consequently, the apparent chlorine dosage dependency observed in Figures 2 and 3 is due primarily to the fact that the free chlorine is completely consumed over five days when the Cl_2/TOC ratio is less than five.

Trussel[18] has noted the same phenomenon with humic acid and divided a curve like Figure 2 into three regions. The first region occurs at low chlorine dosages where immediate chlorine demand is exerted. As Trussel points out, in natural water samples this effect is typically exerted by inorganic species such as ammonia, sulfide, and iron(II). In the case of proteins labile amino acid residues such as lysine, arginine, cysteine, hystidine, and tryptophan are likely to be responsible. Whatever the reactant, addition of chlorine in this region results in limited production of trihalomethanes because of the relatively slow rate of the trihalomethane formation reaction. The second region described by Trussell occurs after the immediate chlorine demand is satisfied. In this region chloroform production is directly proportional to the amount of chlorine added. The amount of chloroform produced is limited because there is not enough chlorine present to fully oxidize the organics to chloroform. At a Cl_2 : TOC ratio of 5 : 1 there is sufficient chlorine present to completely meet the demand needed to produce chloroform and there is comparatively little effect observed by the addition of more chlorine.

Proteins appear to exert a greater chlorine demand per milligram of TOC than humic acid. This is demonstrated in Figure 4 where the total residual chlorine per milligram of TOC is plotted as a function of time for solutions of humic acid and BSA, both of which were initially dosed to 11.9 mg/L chlorine. First of all, there is a much greater demand by the BSA than by the humic acid in the first few hours after dosing. After the first twenty four hours the chlorine dissipation rate levels off to more similar rates for each solution.

It has been reported that increasing the pH of a solution of humic acid dramatically increases the yields of trihalomethanes formed for a specific Cl_2 dose and TOC concentration. BSA also shows a marked increase in yield of chloroform as the pH is raised, especially above pH 9.0 (Figure 5). At pH 10.0 the

Reproduced from
best available copy.

yield from BSA is almost twice that at pH 7.0.

One of the goals of this work was to develop a mathematical model for predicting the yield of trihalomethanes from chlorination of solutions containing known concentrations of proteins. Combined with measured concentrations of proteins in natural waters, this model could be used to predict the contribution proteins make to the trihalomethane formation potential of a given raw water.

The results of time-dependent trihalomethane formation curves for three different levels of BSA at four different initial chlorine dosages were employed as parameters in the algorithm developed by Engerholm and Amy (eq. 2).[17]

$$\ln(CHCl_3) = \ln K + x \ln(TOC) + y \ln(Cl_2/TOC) + z \ln(t) \quad \text{(eq. 2)}$$

In this equation K is a reaction constant which is a function of temperature and pH, TOC is the initial total organic carbon content of the solution in mg/L of precursor, Cl_2 is the initial chlorine concentration in mg/L, and t is the time in hours after dosing. The terms x, y, and z are constants which are characteristic of the particular trihalomethane precursor. In this particular study the reaction temperature was kept constant at 20 °C and the pH was maintained at 7.0 with a 0.025 M phosphate buffer.

The multiregression analysis yielded values of K (.35), x (1.17), y (0.467), and z (0.855) with a correlation coefficient, R^2, of 0.92. The regression was then repeated using a reduced data base, excluding data produced from samples which did not have any residual chlorine at the time of the analysis or which had large standard residuals from the predicted values. These last values corresponded to the data obtained in the first two hours after dosing when the protein is believed to be unfolding. In these first hours the trihalomethane levels are low and the relative error in the measurement is largest. With removal of these points the multiregression analysis yields values of K (1.35), x (0.97), y (0.27), z (0.64) with a correlation coefficient (R^2) of 0.96.

Engerholm and Amy[17] obtained values for a natural humic acid of K (16.8), x (0.95), y (0.28), and z (0.22) under the same conditions of temperature and pH (R^2 = .98). The values Amy obtained for x and y are identical to those we obtained with BSA, while those he calculated for K and z differ dramatically. The similarity of the x values in the two studies is understandable. For limiting concentrations of TOC one might expect the amount of chloroform to double when the concentration of carbon substrate is doubled. The similarity in the value of y obtained for the two substrates was not expected.

The major difference between proteins and humic acid is the rate of the trihalomethane formation reaction. This is supported by the relative importance of the time term in the algorithm for the chloroform production from BSA. The value of z is 0.64 in this expression compared to the value of 0.22 in the equation for the humic acid. This suggests that trihalomethane formation from proteins is much slower than from humic acid. On the other hand, because proteins produce THMs in lower yield than humic acid, they would require a longer incubation time to produce the same THM levels as a similarly concentrated solution of humic acid. Nevertheless, even when this is taken into account, the rate of chloroform formation from proteins is still slower than from humic acid. This can be illustrated in the following manner. Consider a solution of a humic acid which obeys the model developed by Amy. If this solution contains 1.28 mg (as TOC) of humic acid and is chlorinated to a Cl_2/TOC level of six, then after 120 hours (5 days) 100 µg of chloroform will be produced. Because of the lower yield of chloroform per gram of TOC, it requires 2.21 mg of protein to produce 100 µg of chloroform if a solution of BSA which follows our model is chlorinated to a Cl_2/TOC level of six and allowed to sit five days. Even though a higher Cl_2 dose is required to achieve a Cl_2/TOC level of six in the solution of the protein, the two solutions approach the 100 µg maximum at different rates. This difference is illustrated graphically in Figure 6 where it can be seen that the humic acid solution produces far more chloroform in the first twenty four hours than the protein solution.

The objective of developing the model presented here was to measure the relative importance of the contribution of proteins to the overall production of trihalomethanes in a natural water. The model is only an approximation of how proteins may produce trihalomethanes on chlorination. A greater understanding of the distribution of proteins in natural waters is needed before the full significance of their role in the formation of THMs can be determined.

Proteins in Natural Waters

As mentioned earlier, the main source of raw water for the City of Thornton, Colorado is a series of shallow gravel lakes which are adjacent to the S. Platte River one mile downstream from the discharge point of the Denver Metro Wastewater Treatment Plant. Besides periodic groundwater intrusion from the river, the lakes are affected regularly by algae blooms. Throughout the year they are found to be hign in ammonia and dissolved organic nitrogen.

The concentrations of proteins in these lakes were measured regularly from January to June, 1984 and April, 1985 to August, 1985 and intermittantly in between these periods. In general, levels were comparitively low during winter months, as might be expected. There was a slight seasonal variation for one of the lakes, South Gravel Lake, to which no algacide is ever added. A similar phenomenon was observed in the main Gravel Lake during the spring and summer of 1985 (see Table II). In early April and there was a dramatic decrease in protein concentration in the main Gravel Lake following application of copper sulfate as an algacide. Protein concentrations have varied from 0.17 (± .08) mg/L on Feb. 2 to 0.39 (± .04) mg/L on Feb. 22 and 0.31 (± .05) on Mar. 21. During an algae bloom the protein concentration in this lake jumped from an average of about 0.1 mg/L to 0.92 (± .16) mg/L. The highest protein concentration measured in Gravel Lakes occurred on September 11, 1984 when a concentration of 2.26 (± 0.42) mg/L was recorded. Since these levels are measured in mg/L as glycine (molecular weight = 75) and since the molecular weight of the average amino acid in a protein is 120, the approximate weight of protein as BSA can be calculated by multiplying the concentration in mg/L as glycine by 1.6 (i.e., 120/75). Since BSA is 45% carbon by TOC measurement, the weight of proteinaceous carbon is (mg/L as glycine) x 1.6 x 45% = 0.72 x (mg/L as glycine). Therefore, when there was approximately 0.39 (± .04) mg/L of protein (as glycine) in South Gravel Lake on February 22, there was 0.28 mg/L of proteinaceous carbon in South Gravel Lake. There was a total of 5.1 mg/L TOC measured in the lake water sampled on that day. If the assumption is made that there is no unusual interaction between proteins and other organic compounds in the water, then, if the water were chlorinated to a free residual chlorine level of 10 mg/L ($Cl_2/TOC = 2$), after five days (120 hours) the protein would contribute:

$$\mu g \text{ of } CHCl_3 = K\ (\text{Protein as C})^{.97}\ (Cl_2/TOC)^{.27}\ (120)^{.64}$$

or about 10 μg/L.

The City of Thornton is bounded on one side by Lower Clear Creek and on the other by the S. Platte River. Lower Clear Creek contains elevated concentrations of nitrogen and total organic carbon (TOC) because of industrial and municipal wastewater discharge upstream. On February 22, 1984 it contained 4.6 mg/L carbon (TOC) and 0.75 mg/L protein as glycine (0.54 mg/L protein as C). In five days with the same chlorine dose as South Gravel Lake, Lower Clear Creek would produce 20 μg/L of chloroform.

In fact, chlorination of this Lower Clear Creek sample to a one-hour free residual chlorine concentration of 2 ppm produced after five days 54 µg/L of chloroform of which a significant percentage was likely to have been produced by chlorination of proteins.

On February 28, 1984 a study was conducted to determine the effect of different chlorine dosages along a breakpoint curve on the destruction of proteins and the concomitant formation of trihalomethanes over five days (Table III). The sample was collected from one of the gravel lakes which was found to contain approximately 0.38 (± .06) mg/L protein as glycine (0.27 mg/L protein as C) and had a one-hour chlorine demand of about 4 mg/L. The concentrations of trihalomethanes begin to increase dramatically at dosage levels of 5 mg/L and above. However, the protein levels remain relatively constant in samples which contain no free chlorine after five days. When free chlorine is measured in a sample, the protein concentrations begin to decrease. This would seem to suggest that humic acid precursors are oxidized to trihalomethanes before proteins.

In one study water was obtained from a reservoir used as the main water supply for a community in southeastern Pennsylvania. This reservoir is affected by heavy agricultural run-off and was suspected of containing high concentrations of proteins. Water was obtained from several points in the local treatment plant to determine the effect of the different phases of water treatment on the removal of proteins. The utility adds powdered activated carbon to its raw water followed within five minutes by a rapid mix with chlorine and alum and sometimes lime. The water is flocculated for 20 minutes, settled for 4-5 hours, and filtered through a dual medium of sand and anthracite coal. Ammonia is added after filtration followed by lime and chlorine before the water is held in the clear well. A sample of raw water was obtained along with samples of filter effluent and finished water. The samples were dechlorinated with sodium metabisulfite and sealed in glass bottles (Teflon-lined caps) with no headspace. These samples were shipped to Norfolk and analyzed for protein concentrations. The raw water was found to contain 0.96 ± 0.16 mg/L protein as glycine, the filter effluent was found to contain 0.37 ± 0.06 mg/L protein as glycine, and the finished water was found to contain 0.26 ± 0.06 mg/L. It appears that flocculation, sedimentation, and filtration removed slightly more than half of the proteins, but did not remove them completely.

Identification of Amino Acids in Gravel Lakes Water

When the Gravel Lake water was analyzed for amino acids by the OPA method it was anticipated that the concentration of amino acids was approximately 10^{-8} M. This concentration is similar to the concentration of free amino acids found in other natural surface waters. Consequently, a 100-fold concentration would provide a solution with a concentration comparable to that of the solution of standards used. The derivatization method used for the analysis of the amino acids relies on the fact that only compounds containing primary amino groups ($R-NH_2$)

form fluorescent derivatives with OPA.

The chromatogram which was obtained after pre-column derivatization of 10 μL of Gravel Lake concentrate is shown in Fig. 7. The chromatogram obtained after pre-column derivatization of 10 μL of a solution of standard amino acids (10 μM in each) is shown in Fig. 8. A comparison of the chromatograms reveals several facts. First, there are a number of amino compounds in the lake water sample which do not correspond to derivatives of the major amino acid standards. These are likely to be small polypeptides. Secondly, as expected, ammonia, the OPA derivative of which has a retention time of 31 min., is the amino compound with the highest concentration. Because its OPA derivative is considerably less stable than those of the amino acids, it is not possible to quantitate ammonia with significant accuracy by this method. Lastly, the amino acid derivatives which elute between 14 and 25 minutes are superimposed on a large unresolved complex mixture of fluorescent compounds. It is uncertain at this stage what the nature of this mixture is. The compounds which compose the mixture may be amino nitrogen compounds which are derivatized but remain unresolved under the chromatographic conditions used or they may represent other fluorescent compounds in the water. The concentrations of the tentatively identified amino acids are listed in Table IV. These concentrations are slightly higher than those observed for these same amino acids in other freshwater samples, but this is not completely unexpected, since ammonia, TKN, and total organic amino nitrogen concentrations in the sample analyzed are unusually high for a freshwater.

Organic N-Chloramines on Chlorination of Gravel Lakes Water

Water which contains organic amino nitrogen compounds will rapidly form organic N-chloramino compounds, when the water is chlorinated. When the concentrate of Gravel Lake water is chlorinated and incubated for 24 hours and then derivatized with dansyl sulfinic acid, it produces a mixture of fluorescent dansyl amine derivatives which yield the chromatogram shown in Fig. 9. The very large unresolved peak which elutes over the first 15 min. of the chromatogram is due to unreacted dansyl sulfinic acid and dansyl sulfonic acid. The derivative of inorganic N-chloramine (NH_2Cl) has a retention time of 26 min. and dansyl dimethylamine, an artifact of the analysis, has a retention time of 35 min. The remaining peaks are dansyl derivatives of N-chloramino compounds formed on chlorination of the Gravel Lake concentrate. Several of the peaks present in the chromatogram can be correlated with dansyl amino acid standards.

Recently (4/8/85) samples of water were obtained from Gravel Lake and Lower Clear Creek, Thornton, Colorado. These samples have been concentrated 100-fold by freeze-drying, chlorinated to their chloramine maxima (1.5 and 5.0 mg/L, respectively, for the unconcentrated samples and 150 and 500 mg/L after concentration), [illegible] derivatized with dansyl sulfinic acid in the same manner [illegible] sample chromatographed in Fig. 9. Although there are some similarities between the chromatograms obtained from the two samples, the Lower Clear Creek sample has considerably more organic N-chloramines in it than the Gravel Lake sample. The dansyl derivatives are being chromatographed and fractions collected. The eluate from the column will be freeze-dried, rechromatographed to final purity and analyzed by mass spectroscopy using a solids inlet probe in order to identify the compounds present.

CONCLUSION

While the levels of trihalomethanes produced by proteins in these samples are relatively low, it can be seen that their contribution may be quite significant during summer months of high algae growth. In one study it was found that conventional methods of water treatment removed about half of the protein from a raw water sample. Trihalomethanes are only one example of organohalogen compounds which may be produced by chlorination of proteins. More work is needed to investigate the other organohalogen compounds produced.

TABLE I. Yields of Trihalomethanes Formed Five Days After Chlorination of Solutions of Proteins.

Chlorination Substrate	Mol. Wt.	% Carbon	THM's	
			μg/L	% Yield
Bovine Serum Albumin (BSA)	66,000	45	97	0.44
Pepsin	30,000	46	117	0.51
Rennin*	30,000	54	117	0.49
Rennin	30,000	54	47	0.20
Cytochrome C	12,500	45	93	0.42
Humic Acid	unknown	35	135	0.78

*This solution of rennin was not dialyzed.

TABLE II. Seasonal Variation of Protein Concentrations in Gravel Lakes and Lower Clear Creek, Thornton, Colorado During the Spring and Summer, 1985.

	PROTEIN CONCENTRATION (mg/L as Glycine)	
DATE	GRAVEL LAKE	LOWER CLEAR CREEK
4-8-1985	0.25 (±0.08)	0.62 (± 0.10)
5-13-1985	0.39 (±0.11)	0.37 (± 0.10)
5-28-1985	0.57 (±0.09)	0.27 (± 0.10)
6-24-1985	1.03 (±0.23)	0.53 (± 0.12)
7-8-1985	0.52 (±0.10)	0.50 (± 0.07)
8-6-1985	0.59 (±0.09)	0.84 (± 0.18)
8-17-1985	—	0.30 (±0.09)

TABLE III. Protein Concentrations and 5-Day Terminal Trihalomethane Concentrations Produced from Chlorination of Raw Water from Gravel Lakes @ Well 28, Thornton, CO.

CHLORINE DOSE (mg/L)	RESIDUAL CHLORINE (mg/L)	5-DAY TTHM (µg/L)	PROTEIN (mg/L as glycine)
0	0	-	.38 ± .06
2	0	26	.42 ± .05
5	0	169	.32 ± .04
7	0	217	.41 ± .07
10	.6	274	.29 + .05
12	1.8	286	.19 ± .02

Table IV. Amino Acids Tentatively Identified in Gravel Lake Water (9/11/84) as Their OPA Derivatives.

Retention Time (minutes)	Identification[a] of Amino Acid	μg/L in Unconcentrated Gravel Lakes Water
7.59	Aspartic Acid[b]	5.0
7.8	Aspartic Acid[b]	10.2
9.33	Glutamic Acid	14.6
14.48	Serine	16.6
17.05	Threonine	--
18.85	Alanine	19.0
23.71	Valine	12.6
30.65	Ammonia	--

---

[a] Tentative identification based on correlation of retention time of peaks with those of known standards.

[b] It was not possible to distinguish which peak correctly correlated with that of aspartic acid.

REFERENCES

1. Gocke, K. "Untersuchungen uber Abgabe und Aufname von Aminosauren und Polypeptiden durch Plankton-organismen," *Arch. Hydrobiol.* 67:285-367 (1970).
2. Tuschall, J. R., Jr. and P. L. Brezonik. "Characterization of Organic Nitrogen in Natural Waters: Its Molecular Size, Protein Content and Interactions with Heavy Metals," *Limnol. Oceanogr.* 25(3):495-504 (1980).
3. Speed, M., unpublished results.
4. Stanbro, W. D. "The Chemistry of Amino Acids and Peptides in Power Plant Cooling Towers," *Ches. Science* 18(1):126-128 (1977).
5. Ram, N. M. and J. C. Morris. "Environmental Significance of Nitrogenous Organic Compounds in Aquatic Sources," *Environment Int'l* 4:397-405 (1980).
6. Manny, B. A. "Seasonal Changes in Dissolved Organic Nitrogen in Six Michigan Lakes," *Verh. Internat. Verein. Limnol.* 18:147-156 (1972).
7. Gardner, W. S. and J. A. Stephens. "Stability and Composition of Terrestrially Derived Dissolved Organic Nitrogen in Continental Shelf Surface Waters," *Marine Chemistry* 6:335-342 (1978).
8. Gardner, W. S. and G. F. Lee. "The Role of Amino Acids in the Nitrogen Cycle of Lake Mendota," *Limnol. Oceanogr.* 20(3):379-388 (1975).
9. Williams, D. B. "The Organic Nitrogen Problem," *J. Amer.*

Water Works Assn. 43:837-846 (1951).

10. Oliver, B. G. and D. B. Shindler. "Trihalomethanes from the Chlorination of Aquatic Algae," *Environ. Sci. & Technol.* 14:1502-1505 (1980).

11. Hoehn, R. C., D. B. Barnes, B. C. Thompson, C. W. Randall, T. J. Grizzard, and P. T. B. Shaffer. "Algae as Sources of Trihalomethane Precursors," *J. Amer. Water Works Assn.* 72:344-350 (1980).

12. Hoehn, R. C., K. L. Dixon, J. K. Malone, J. T. Novak, and C. W. Randall. "Biologically Induced Variations in the Nature and Removability of THM Precursors by Alum Treatment," *J. Amer. Water Works Assn.* 76:134-141 (1984).

13. Morris, J. C., N. M. Ram, B. Baum, and E. Wajon. "Formation and Significance of N-Chloro Compounds in Water Supplies," EPA 600/2-80-031 (Cincinnati, OH: Municipal Environmental Research Laboratory, Office of Research and Development, 1980).

14. "Analysis of Trihalomethanes in Drinking Water. Appendix C - Part II," *Federal Register.* 44(231):68683-68690 (1979).

15. Westall, F. and H. Hesser. "Fifteen-Minute Acid Hydrolysis of Peptides," *Anal. Biochem.* 61:610-613 (1974).

16. Fogg, G. E., W. D. P. Stewart, P. Fay, and A. E. Walsby. *The Blue-Green Algae* (London: Academic Press, Inc., 1973), pp. 49-51.

17. Engerholm, B. A. and G. L. Amy. "A Predictive Model for Chloroform Formation from Humic Acid," *J. Amer. Water Works Assn.* 75:418-423 (1983).

18. Trussel, R. R. and M. D. Umphres. "The Formation of Trihalomethanes" *J. Amer. Water Works Assn.* 70:604-612 (1978).

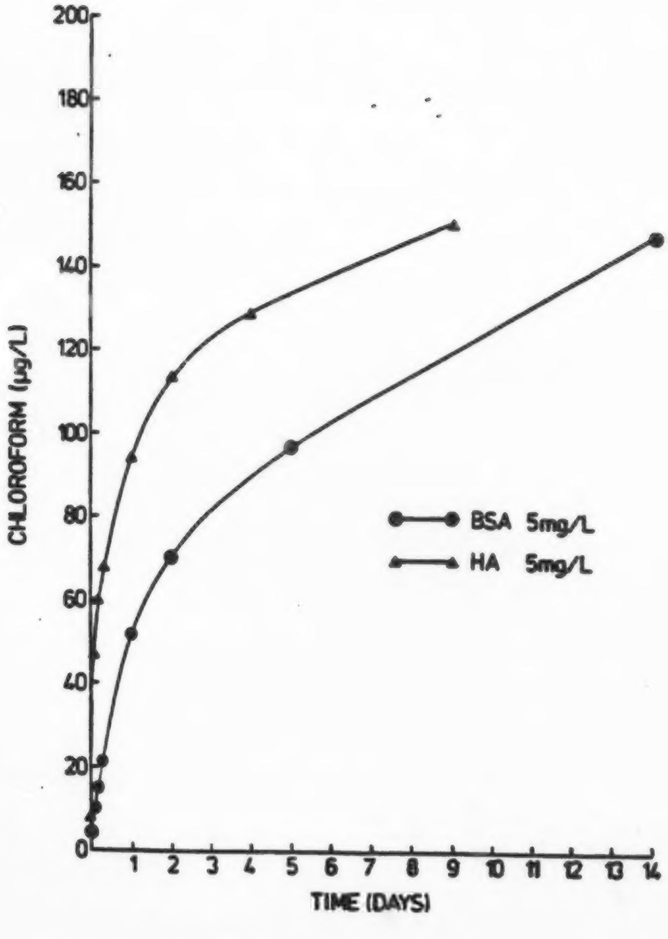


Figure 1. The amount of chloroform produced with time after solutions of 5 mg/L BSA (2.2 mg/L as C) or 5 mg/L humic acid (1.7 mg/L as C), both in 0.025 M aqueous potassium phosphate at pH 7.0, were chlorinated to 20 mg/L Cl_2 and incubated in the dark at 20 ($\pm$0.5)°C.

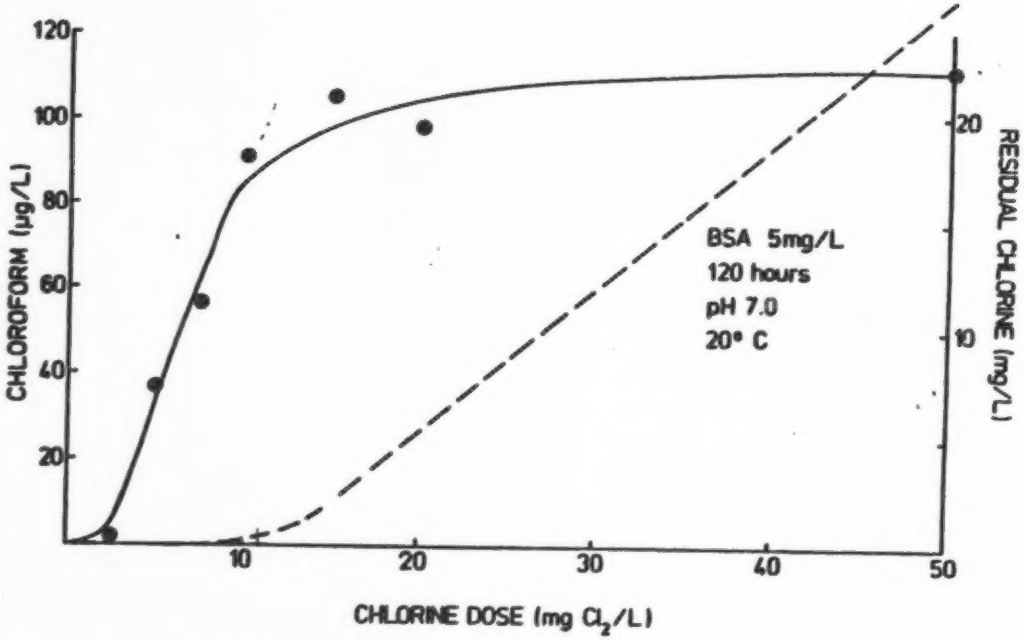


Figure 2. Chloroform produced and residual chlorine remaining 120 hours after a solution of 5 mg/L BSA (2.2 mg/L as C) in 0.025 M aqueous potassium phosphate (pH 7.0) was chlorinated to various levels and stored in the dark in a constant temperature bath at 20 (±0.5) °C.

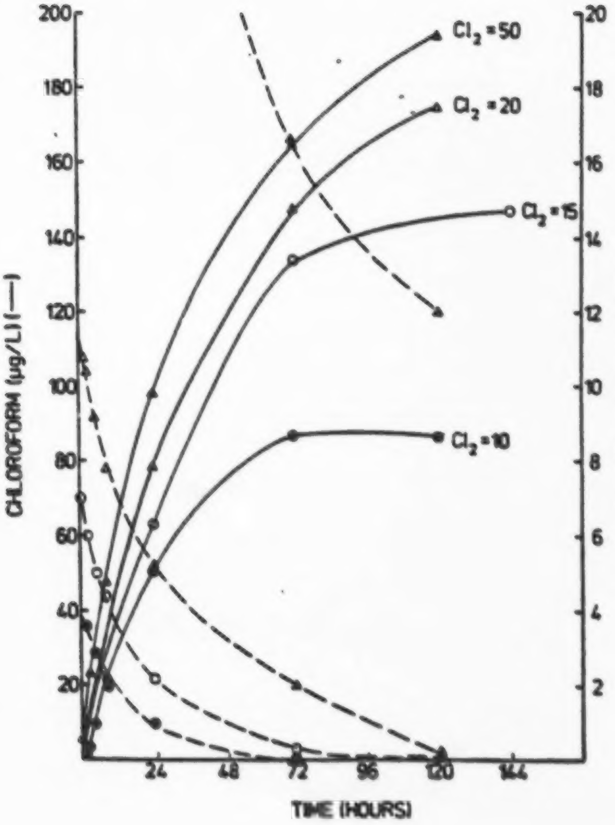


Figure 3. The amount of chloroform produced and the corresponding total residual chlorine remaining at various times after solutions of 10 mg/L BSA (4.4 mg/L as C) in 0.025 M aqueous potassium phosphate at pH 7.0 were chlorinated to varying chlorine concentrations and incubated in the dark at 20 (±0.5) °C.

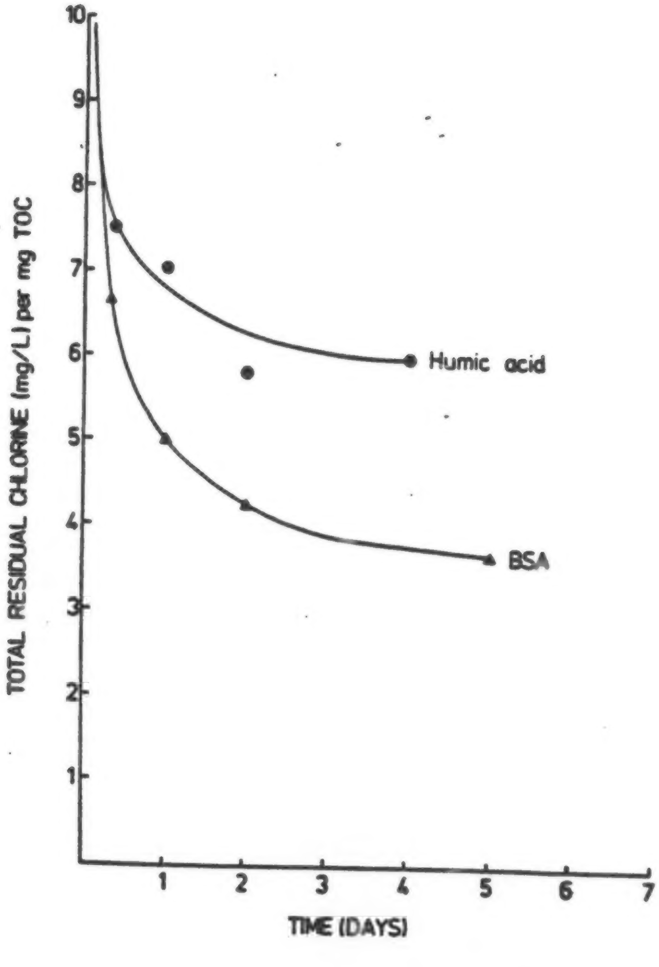


Figure 4. The residual chlorine remaining at varying times after solutions of humic acid (1 mg/L as C) or BSA (1 mg/L as C), both in 0.025 M potassium phosphate buffer at pH 7.0, were chlorinated to 11.9 mg/L Cl_2 and stored in the dark at 20 (±0.5) °C before being analyzed.

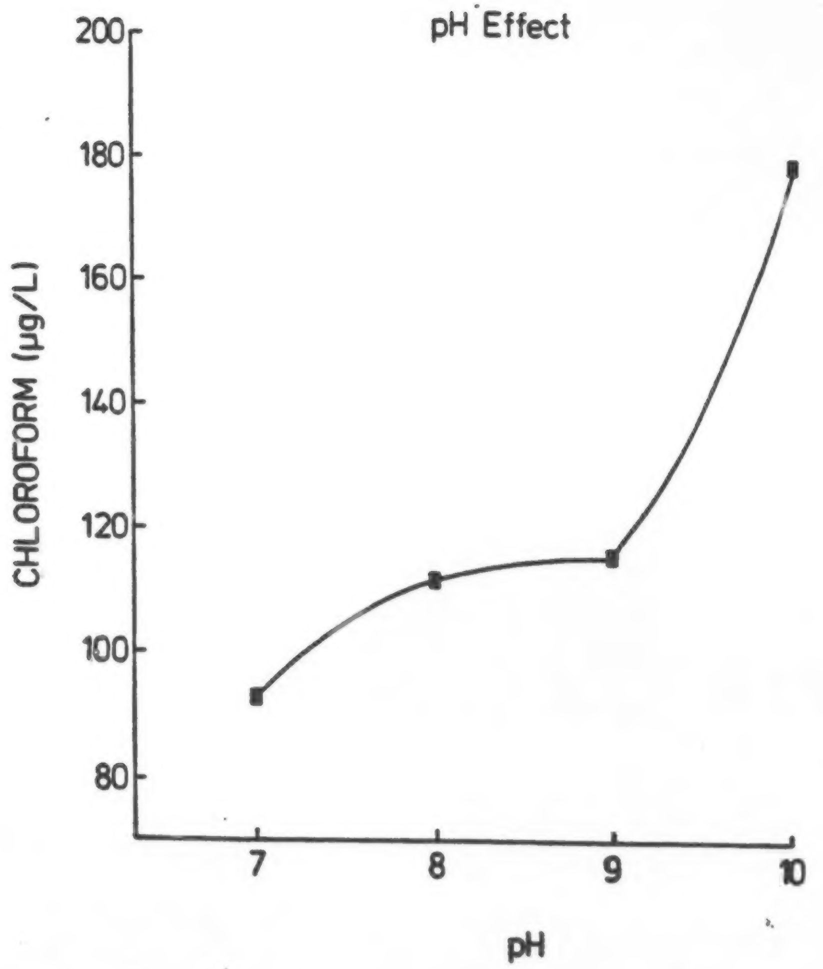


Figure 5. The yield of chloroform obtained five days after solutions of 5 mg/L BSA in 0.025 M aqueous potassium phosphate (pH 7.0 and 8.0) or in 0.025 M aqueous sodium borate (pH 9.0 and 10.0) were chlorinated to 20 mg/L Cl_2 and incubated in the dark at 20 (±0.5) °C.

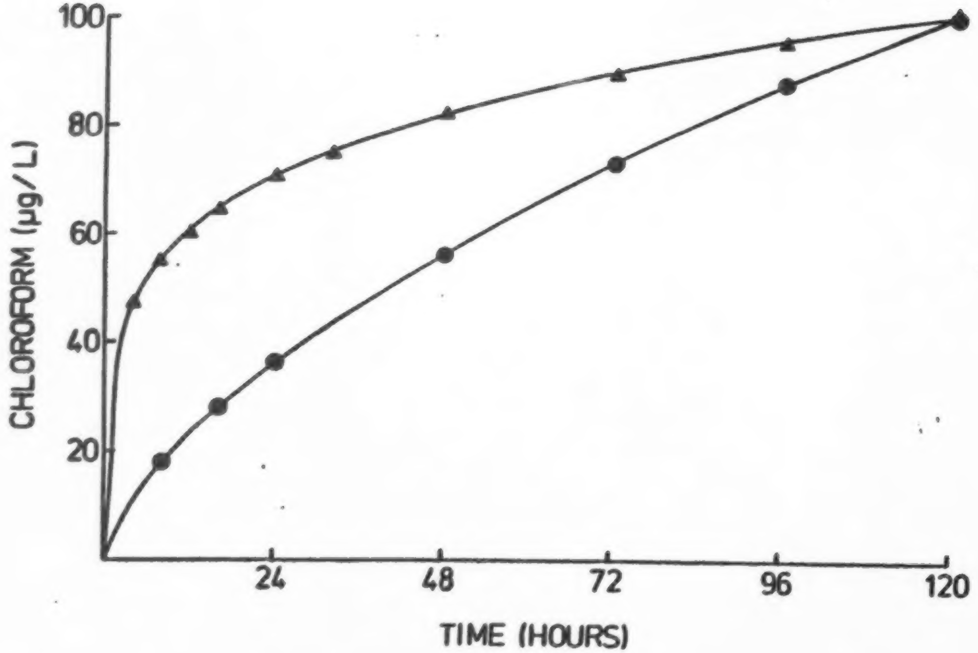


Figure 6. The predicted yield of chloroform with time from solutions of humic acid (▲-----▲, 1.28 mg/L as C) and BSA (●-----●, 2.21 mg/L as C), both in 0.025 M aqueous potassium phosphate at pH 7.0 assuming an initial Cl_2/TOC level of 6. The algorithm of Amy was used to generate the curve for humic acid and the algorithm developed in the current study was used to generate the curve for BSA.

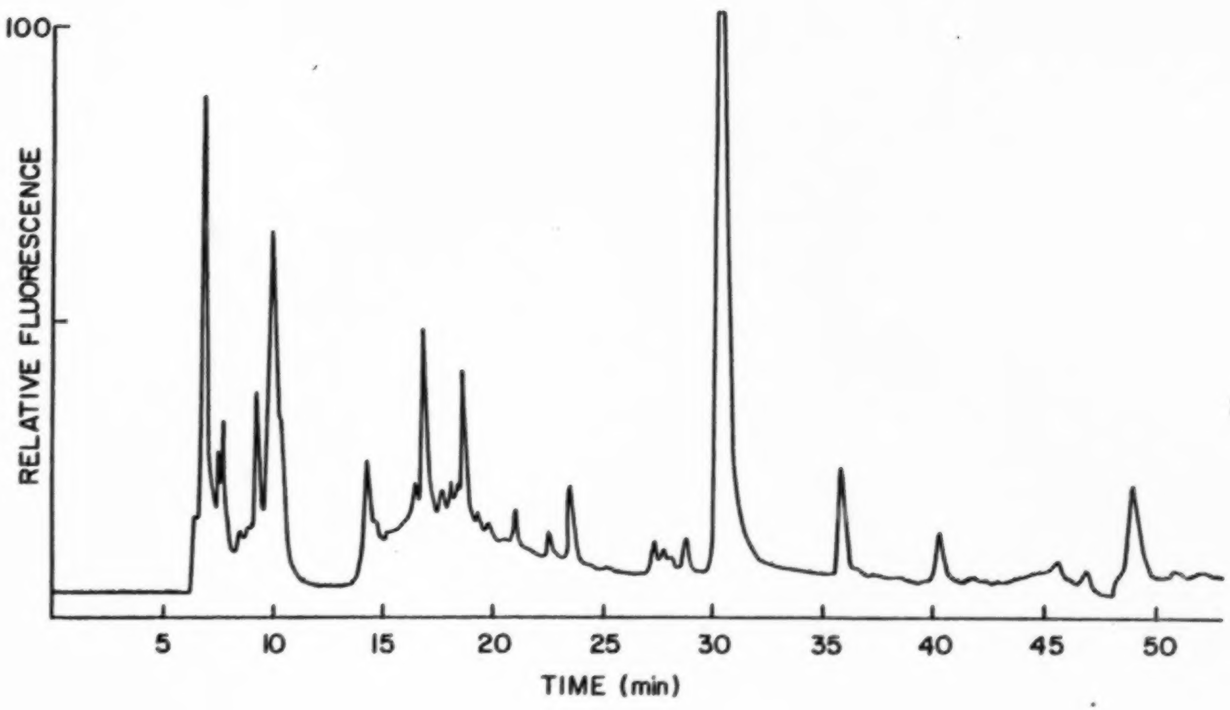


Figure 7. Liquid chromatogram of fluorescent OPA derivatives of amino nitrogen compounds in Gravel Lake water concentrated 100-fold by freeze-drying.

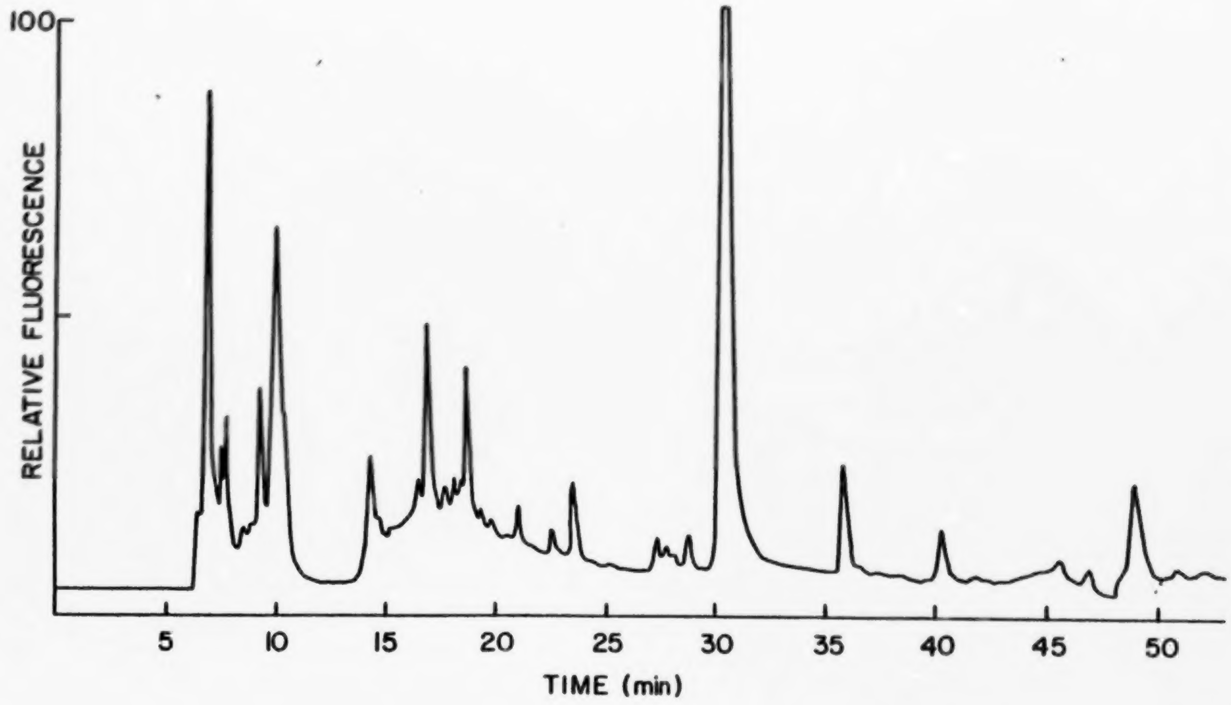
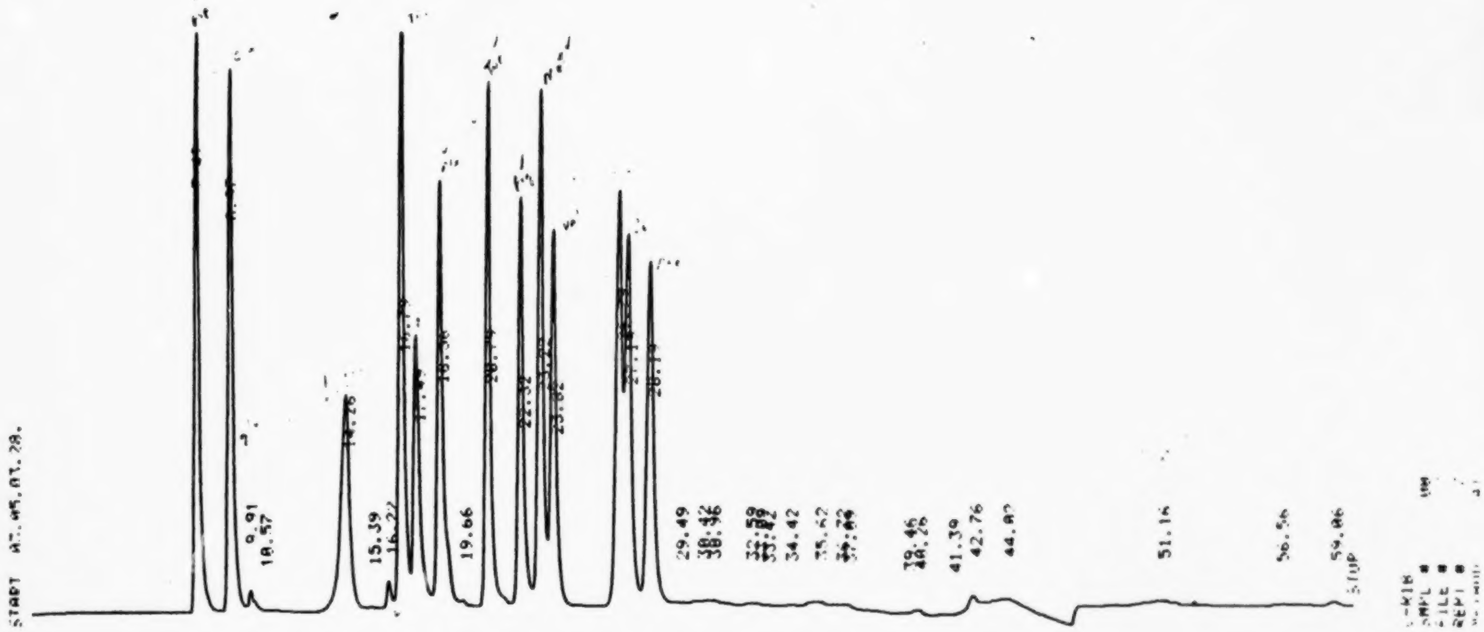


Figure 8. Liquid chromatogram of fluorescent OPA derivatives of amino nitrogen compounds in Gravel Lake water concentrated 100-fold by freeze-drying.



Reproduced from best available copy.

Figure 9. Liquid chromatogram of fluorescent OPA derivatives of a standard mixture of amino acids (10 uM). Sample size = 10 uL.

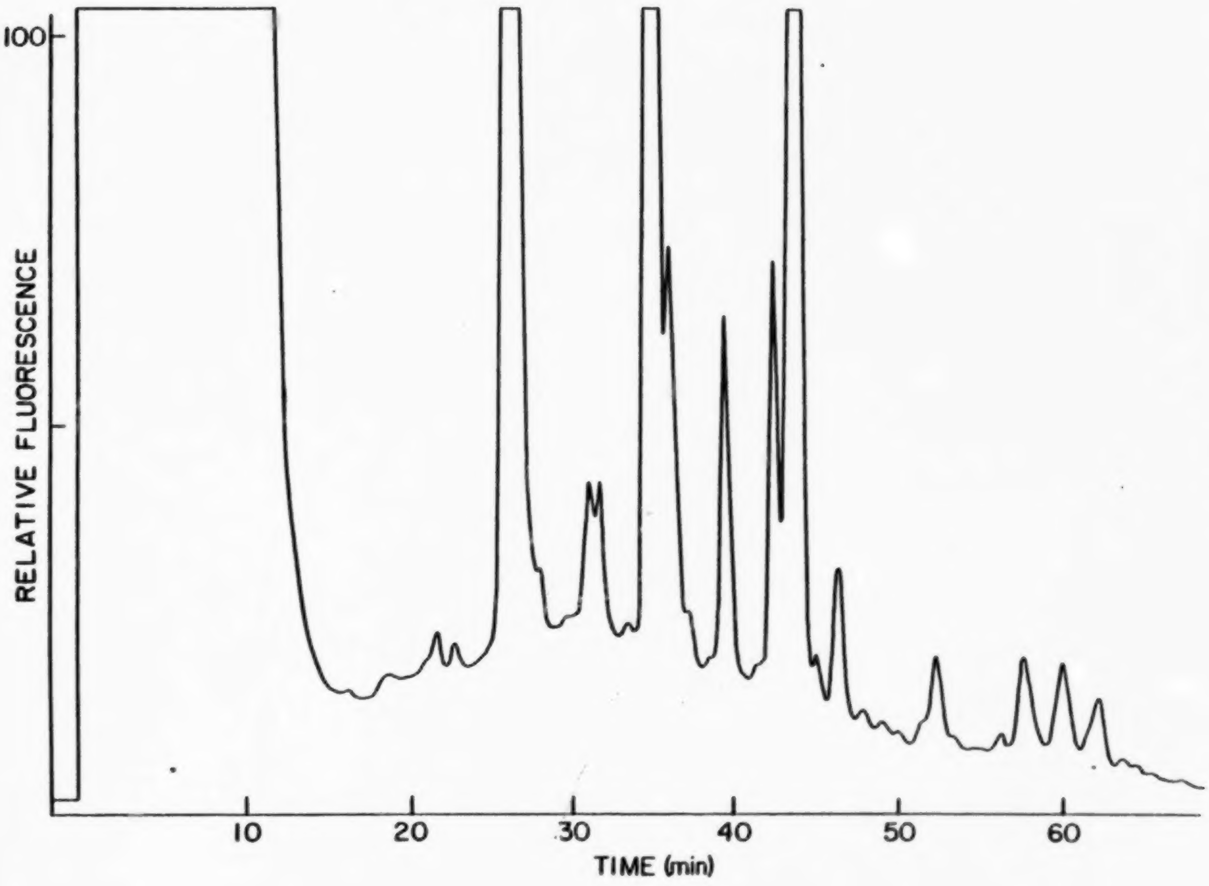


Figure 10. Liquid chromatogram of dansyl derivatives of organic N-chloramines formed by chlorination of a 100-fold concentrate of water from Gravel Lake, Thornton, Colorado sampled on 9/11/85.